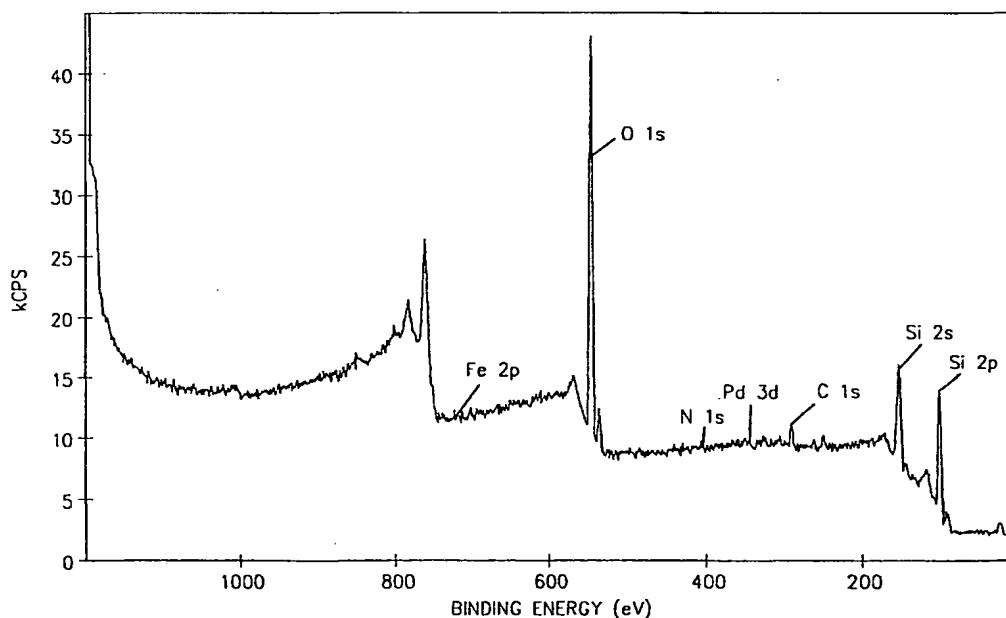




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: ROOM TEMPERATURE WET CHEMICAL GROWTH PROCESS OF SiO BASED OXIDES ON SILICON



## (57) Abstract

Disclosed is a room temperature wet chemical growth (RTWCG) process of SiO<sub>2</sub>-based insulator coatings on silicon substrates for electronic and photonic (optoelectronic) device applications. The process includes soaking the Si substrates into the growth solution. The process utilizes a mixture of H<sub>2</sub>SiF<sub>6</sub>, N-n-butylpyridinium chloride, redox Fe<sup>2+</sup>/Fe<sup>3+</sup> aqueous solutions, and a homogenous catalyst.

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ROOM TEMPERATURE WET CHEMICAL GROWTH PROCESS OF  
SiO BASED OXIDES ON SILICON

BACKGROUND OF THE INVENTION

This invention relates to a room temperature wet chemical growth (RTWCG) process of SiO-based insulator coatings on semiconductor substrates including Si, Ge, III-V and I-III-VI compound semiconductors and, specifically, to the RTWCG of SiO-based films on Si in the manufacture of silicon-based electronic and photonic (optoelectronic) device applications.

The United States Government has rights in this invention pursuant to NASA Contract No. NAS3-97181.

Silicon dioxide (SiO<sub>2</sub>) forms the basis of the planar technology. In industrial practice insulator coatings for electronic and photonic devices layers are most frequently formed by thermal oxidation of Silicon (Si) in the temperature range 900 to 1200°C. SiO<sub>2</sub> is also deposited by chemical vapor deposition (CVD) techniques at lower temperatures (200 to 900°C) on various substrates.

Thermal and CVD-grown SiO<sub>2</sub> based layers are used as diffusion masks, to passivate device junctions, as electric insulation, as dielectric material in Si technology, and as capping layers for implantation-activation annealing in III-V compound semiconductor technology, to name a few.

The growth of insulator films at low temperatures is very attractive for most device applications due to reduced capital cost, and high output and technological constraints associated with the growth of dielectric thin films using conventional high-temperature growth/deposition techniques.

Dielectric films for photonic devices are well known in the art and are usually deposited at near room temperature on various substrates using physical vapor deposition processes including conventional (nonreactive) or reactive resistive, induction or electron beam evaporation, reactive or nonreactive dc or RF

1 magnetron and ion-beam sputtering processes.

2 Room temperature growth of insulator layers on semiconductor  
3 surfaces using anodic oxidation is known in the art. For silicon,  
4 using anodic oxidation up to 200 nm  $\text{SiO}_2$  layers can be grown on  
5 the underlying Si substrates. The anodic oxidation process  
6 consumes about 0.43 of the thickness of the oxide from the  
7 underlying Si substrate, and is not compatible with most  
8 metallization schemes. This limits its application as a  
9 replacement of thermal or vacuum deposited  $\text{SiO}_2$ .

10 Deposition of  $\text{SiO}_2$  insulator layers from solutions is known  
11 in the art using organo-metallic solutions. In this procedure,  
12 the insulator layer is applied onto the substrate either by  
13 dipping the substrate into the solution or by spinning the  
14 substrate after a small amount of the solution is applied onto  
15 the surface. In both cases the substrate is then placed in an  
16 oven to drive off the solvent.

17 Researchers from Japan, China and Taiwan describe processes  
18 for deposition of  $\text{SiO}_2$  and  $\text{SiO}_{2-x}\text{F}_x$  layers on glass and silicon  
19 surfaces using a room temperature (30 to 50°C) solution growth.  
20 The growth of liquid-phase deposited (LPD)  $\text{SiO}_2$ , initially  
21 proposed by Thomsen et al. for deposition of  $\text{SiO}_2$  on the surface  
22 of soda lime silicate glass, is based on the chemical reaction  
23 of  $\text{H}_2\text{SiF}_6$  with water to form hydrofluoric acid and solid  $\text{SiO}_2$ . The  
24 initial  $\text{H}_2\text{SiF}_6$  solution is saturated with  $\text{SiO}_2$  powder (usually in  
25 a sol-gel form). Before immersing the glass into the solution,  
26 a reagent that reacts with the hydrofluorosilicic acid, such  
27 as boric acid, was added to the solution. Boric acid reacts with  
28 the hydrofluorosilicic acid and makes the solution  
29 supersaturated with silica.

30 One of the major disadvantages of  $\text{SiO}_2$  LPD method described  
31 above is a very low deposition rate of about 8 nm/hour to about  
32 24 nm/hour, which makes it impractical for growing insulator  
33 layers for most semiconductor device applications. Deposition  
34 rates of up to 110 nm/hour are claimed by Ching-Fa Yeh et al. in  
35 the hydrofluorosilicic acid-water system and the composition

1 of the resulting films was reported to be  $\text{SiO}_{2-x}\text{F}_x$  where x is  
2 about 2%. Our own experimentation using the LPD method, seems to  
3 indicate that the LPD  $\text{SiO}_2$  has poor adhesion to the Si surfaces,  
4 and the maximum growth rate we obtained is smaller than the  
5 reported values (less than 25 nm/hour). Even assuming that the  
6 reported 110 nm/hour deposition rates are possible, these  
7 deposition rates are still too low since assuming that the  
8 deposition rate is constant with the deposition time, it will  
9 require about 9 hours to deposit an oxide with a thickness of  
10 about 1  $\mu\text{m}$  needed for ULSI interlevel dielectric.

11 The term RTWCG process of SiO-based insulator layers as used  
12 herein means a room temperature (e.g., 10°C-40°C) wet chemical  
13 growth process of  $\text{Si}_x\text{O}_y\text{X}_z$  ( $\text{SiOX}$ ) layers where x is from 0.9 to  
14 1.1, y is from 0.9 to 1.9 and z is from 0.01 to 0.2, where Si  
15 stands for silicon, O stands for oxygen, and X is either fluorine  
16 (F), carbon (C) or a combination of these with iron (Fe),  
17 palladium (Pd), or titanium (Ti) contaminants, depending on the  
18 redox system being used.

#### 19 SUMMARY OF THE INVENTION

20 This invention relates to a room temperature wet chemical  
21 growth (RTWCG) process of silicon oxide ( $\text{SiO}$ ) based thin film  
22 dielectrics on semiconductor substrates and, specifically, to the  
23 RTWCG of SiO-based films on silicon in the manufacture of  
24 silicon-based electronic and photonic (optoelectronic) device  
25 applications.

26 It is an object of the invention to provide a silicon  
27 oxide-based film using a room temperature wet chemical growth  
28 (RTWCG) process for electronic and photonic (optoelectronic)  
29 device applications that is compatible with device fabrication  
30 steps, has large growth rates, low stress, good adhesion to  
31 silicon and silicon oxide coated surfaces, is stable on long term  
32 air exposure, and high temperature annealing, and that has very  
33 good conformity.

1           It is a further object to provide a silicon oxide-based  
2 RTWCG process of low dielectric constant SiO based films for use  
3 as intermetallic dielectric (IMD) and interlevel dielectric (ILD)  
4 in ultra large scale integrated (ULSI) silicon based  
5 microelectronics.

6           It is a further object to provide an ultra thin film silicon  
7 oxide-based RTWCG process to be used as gate dielectric for ULSI  
8 silicon based microelectronics.

9           It is a further object to provide a silicon oxide-based  
10 RTWCG process of thin film insulators to be used as passivation  
11 layers for photonic (optoelectronic) device applications.

12           It is a further object to provide a silicon oxide-based  
13 RTWCG process to grow passivating/antireflection coatings, after  
14 the front grid metallization for the fabrication of low cost  
15 silicon solar cells and for other photonic (optoelectronic)  
16 device applications.

17           It is a further object to provide a silicon oxide-based  
18 RTWCG deposition process to be used as passivating films for  
19 porous silicon coated photonic (optoelectronic) devices.

20           High growth rates of SiOX oxides according to this invention  
21 are grown on planar or porous silicon using commercial grade  
22  $\text{H}_2\text{SiF}_6$  (34%) as silicon source, N-n-butylpyridinium chloride  
23 ( $\text{C}_9\text{H}_{14}\text{ClN}$ ) and redox aqueous solutions based on  $\text{Fe}^{2+}/\text{Fe}^{3+}$ , e.g.,  
24  $\text{K}_3\text{Fe}(\text{CN})_6$ , and Iron Ethylenediaminetetraacetic acid (Fe EDTA).  
25 For convenience the above class of solutions we are going to call  
26 the basic growth solution. The basic solution (BS) can be  
27 saturated with  $\text{SiO}_2$ -containing sources such as silica gel.  
28 Catalysts such as palladium II trifluoroacetate [ $\text{Pd}(\text{O}_2\text{C}_2\text{F}_3)_2$ ]  
29 (PdFAC) and  $\text{H}_2\text{TiF}_6$  aqueous solutions are used to increase the  
30 growth rate. NaOH, KOH, NaF and  $\text{NH}_4\text{F}$  and HF solutions are used  
31 according to this invention to adjust the pH of the growth  
32 solution. The RTWCG rate on Si surfaces is from 2 nm/minute to  
33 64 nm/minute, depending on the composition of the solution, pH,  
34 and crystallographic orientation of the Si substrates. The  
35 chemical composition of the grown layer has the general formula:

1  $\text{Si}_x\text{O}_y\text{X}_z$ , where the significance of Si, O, X, and x, y and z are  
2 as explained above.

### 3 BRIEF DESCRIPTION OF THE DRAWINGS

4 The foregoing and other objects, features and advantages of  
5 the invention will be apparent from the following more particular  
6 description of preferred embodiments of the invention, as  
7 illustrated in the accompanying drawings.

8 Fig. 1 is a XPS surface survey of an RTWCG SiOX oxide (89  
9 nm thick), grown on (111) p-type Si:B in A4:Pd solution, after  
10 sputtering of about 30 nm from the surface.

11 Fig. 2 is a XPS surface survey of an RTWCG SiOX oxide (112  
12 nm thick), grown on p-type Si in BS:B15 solution, after the  
13 removal of about 3 nm from the surface.

14 Fig. 3 is a XPS surface survey of an RTWCG SiOX oxide (about  
15 12 nm thick), grown on p-type Si in BS:B19 solution.

16 Fig. 4 is a depth profile of oxide in Fig. 3.

17 Fig. 5 is a XPS surface survey of an RTWCG SiOX oxide, grown  
18 on p-type porous Si in BS:PS6 solution.

19 Fig. 6 is a XPS surface survey of an RTWCG SiOX oxide (235  
20 nm thick), grown on p-type Si in BS-Ti34 solution, after the  
21 removal of about 13 nm from the surface.

22 Fig. 7a and Fig. 7b are clasp views of Ti and Fe windows in  
23 the survey in Fig. 6.

24 Fig. 8 are plots of index of refraction against wavelength  
25 for selected RTWCG SiOX-based thin film oxide layers grown on  
26 (111) p-type silicon substrates.

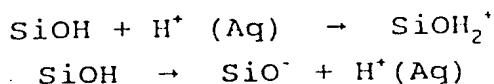
27 Fig. 9 are plots of external quantum efficiency against  
28 wavelength for a  $4\text{cm}^2$  Si solar cell with (a) bare and (b) RTWCG  
29 SiOX-based AR coating.

30 Fig. 10 are plots of reflectivity against wavelength of (a)  
31 RCA cleaned (100) p-type Si, (b) PS coated, (c) RTWCG SiOX  
32 passivated PS using a solution A4-Pd, (d) RTWCG SiOX oxide using

1 a solution BS-PS6.

2 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

3 Surface OH groups are known in the art as one of the most  
4 important sites for chemical reactions at oxide surfaces. The OH  
5 groups are formed by the chemisorption of water molecules on the  
6 oxide surface. The hydration mechanism involves the dissociation  
7 of an adsorbed water molecule, where an  $H^+$  ion bonds to an oxygen  
8 ion on the surface and an  $OH^-$  ion bonds to a silicon ion on the  
9 surface. The SiOH groups can undergo acid or base reactions. They  
10 accept a hydrogen ion to become an  $SiOH_2^+$  site having a positive  
11 charge, or they release a hydrogen ion to become  $SiO^-$  site having  
12 a negative charge. The reactions are written as:



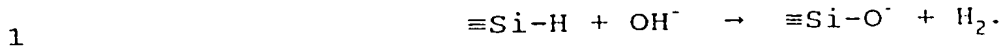
13  
14  
15 The concentration of the  $SiOH_2^+$  and  $SiO^-$  species depend on  
16 the pH of the aqueous phase. The  $SiOH_2^+$  species increases at  
17  $pH < 7$ , while the  $SiO^-$  species increases at  $pH > 7$ .

18 After the RCA clean and prior to the final water rinse, the  
19 silicon surface is passivated by  $\equiv Si-H$  and  $\equiv Si-F$  bonds. We define  
20 the "induction time" as the time interval  $dt = t_{ox} - t_{in}$ , where  $t_{ox}$   
21 is the time referenced to the initial time ( $t_{in}$ ) after which the  
22 oxide deposition is initiated. For HF treated surfaces we found  
23 an induction time from 10 seconds to 2 minutes. On contrary, on  
24 similar silicon samples covered either with a thin native oxide  
25 (no RCA clean) or thermally grown  $SiO_2$  layers, the induction time  
26 is from about 10 to 20 seconds.

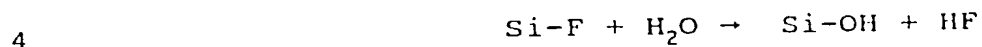
27 Prior to the initiation of the RTWCG of SiOX-based layer,  
28 for hydrogen- or fluorine-terminated Si surfaces the Si-H and  
29 Si-F bonds has to be converted into the Si-OH bonding group.

30 The hydration mechanism of hydrogen passivated surfaces  
31 should follow the reaction:

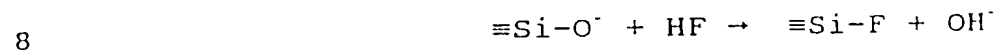




2 For  $\equiv\text{Si-F}$  terminated bonds, rinsing the samples in water  
3 allows the  $\text{Si-F} \rightarrow \text{Si-OH}$  to take place according to the reaction:



5 From the last two reactions, it is apparent that in the  
6 presence of HF, the surface may be subject to HF attack through  
7 HF insertion into the Si-O bond, according to the reaction:



9 with the subsequent removal of the surface Si atom from the  
10 surface of the underlying Si-O oxide.

11 We found that after the HF dip, rinsing the substrates in  
12 deionized water for 5 to 10 minutes or into 0.1%  $\text{H}_2\text{O}_2$  for 1 to 2  
13 minutes, depending on the crystallographic orientation, doping  
14 type and majority carrier concentration, the induction time for  
15 all silicon substrates was below 20 seconds.

16 Once the growth of a native oxide layer has began, Si-H and  
17 Si-F bonds are replaced by the Si-OH bonds. These Si-OH groups  
18 in turn facilitate the incorporation from the growth solution of  
19 silicon and oxygen by forming Si-O-Si bond angles. Associated  
20 Si-OH groups also act as preferential adsorption sites for water  
21 molecules further speeding up oxygen and silicon incorporation  
22 process.

23 In designing the room temperature RTWCG process of SiOX  
24 dielectric layers, we imposed the following conditions:

25 the use of elements, which are known to harm the  
26 semiconductor devices, should be avoided; only Si (O,  
27 C, H, and N) are acceptable.

28 for growing SiOX oxides, metal impurities such as Mg, Ti,  
29 and Ta, which are known to introduce large density of  
30 states at the Si/insulator interface,

1           should be avoided.

2           the SiOX films should be stable in reducing and oxidizing  
3           atmosphere, with respect to factors such as heat,  
4           humidity, prolonged exposure to UV light, atomic  
5           oxygen and ionizing radiation such as high energy  
6           electrons and protons.

7           the SiOX films should have contamination-free bonding to  
8           the Si surfaces and sufficient mechanical strength.

9           the growth process should be applicable to any Si surface,  
10          irrespective of crystal orientation, size and shape.

11          the growth process should be compatible with processing  
12          sequences of advanced Si devices, e.g. VLSI  
13          microelectronics with critical features below 0.25  $\mu\text{m}$ .

14          High deposition rate of SiOX oxides are deposited using  
15          commercial grade  $\text{H}_2\text{SiF}_6$  (34%) as silicon source, n-n  
16          butyldipyrrinium chloride (n-BPCL) and redox  $\text{Fe}^{2+}/\text{Fe}^{3+}$  (10%) such  
17          as  $\text{K}_3\text{Fe}(\text{CN})_6$  (KFeCN) and Fe EDTA aqueous solutions. In a  
18          preferred embodiment of the invention, the growth solution is  
19          made by mixing 2 to 5 volume parts of 34%  $\text{H}_2\text{SiF}_6$  (HSiF) with 2 to  
20          5 volume parts of 0.5 M KFeCN aqueous solution and 0 to 4 volume  
21          parts of 5% n-BPCL aqueous solution. This solution, for  
22          convenience we are going to call: "the basic solution (BS)." The  
23          BS can be saturated with  $\text{SiO}_2$ -containing sources such as silica  
24          gel or with  $(\text{NH}_4)_2\text{SiF}_6$ . Catalysts such as palladium II  
25          trifluoroacetate  $\text{Pd}(\text{O}_2\text{C}_2\text{F}_3)_2$  (PdFAC) are adequate for mild acidic  
26          solutions (pH from 4 to 6).  $\text{Ti}^{4+}$ - based aqueous solutions such  
27          as hexafluorotitanate  $\text{H}_2\text{TiF}_6$  (HTiF), titanium chloride  $\text{TiCl}_4$   
28          ( $\text{TiCl}$ ) and  $(\text{NH}_4)_2\text{TiF}_6$  (NHTiF) we found to be adequate catalysts  
29          for the growth in aqueous solutions (pH from 3 to 8), and its use  
30          sensitively increases the SiOX RTWCG rate. NaF, KOH, NaF and  
31           $\text{NH}_4\text{F}$  solutions are used according to this invention to adjust the  
32          pH of the growth solution between 3 and 10.

33          The volume of the growth solution is from 0.2 ml to 0.6  
34          ml/cm<sup>2</sup> of the Si surface which comes in contact with the  
35          solution (not including the portions of the surface covered by

1 photoresist) for a SiOX oxide thickness of 0.1 to 0.25  $\mu\text{m}$ . For  
2 best results, the solution is agitated by any practical means  
3 until the solids are completely dissolved, and during the RTWCG  
4 so as to ensure uniform coating.

5 In Fig. 1 is given a XPS surface survey of an RTWCG SiOX  
6 oxide, grown on (111) p-type Si:B with  $(N_A - N_D)$  of about  $2 \times 10^{19} \text{ cm}^{-3}$   
7 using the A4:Pd solution, after sputtering of about 30 nm from  
8 the surface. The composition of the A4:Pd RTWCG solution is: 5  
9 volume parts of 34% HSiF, 3 volume parts of 5% n-BPCl, 2 volume  
10 parts of 30% HNO<sub>3</sub> solution, 1 volume part CH<sub>3</sub>COOH, 0.1 grams of  
11 KFeCN and 10 mg of PdFAC.

12 Prior to the growth, the solution was stirred using an  
13 magnetic agitator for 10 minutes. The surface of the Si substrate  
14 was cleaned using the standard RCA clean, and rinsed in deionized  
15 (DI) water for 10 minutes. After 3 minutes, in the dark, the  
16 thickness of the oxide measured by ellipsometry was 89 nm, which  
17 corresponds to a growth rate of about 30 nm/min. However, for  
18 longer growth times, the growth rate decreases, reaching about  
19 12 nm/min, after 10 minutes growth time. The thickness of the  
20 underlying substrate removed during the growth was about 20 nm  
21 for the 89 nm thick oxide and of about 32 nm for the 123 nm thick  
22 oxide. In both cases this is about 25% of the oxide thickness.  
23 This means that the oxide formation process is not a simple  
24 chemical oxidation, since in this case the thickness of the  
25 removed layer from the Si surface should be at least 43% the  
26 thickness of the oxide. The oxide formation in this case is a  
27 dual chemical oxidation and growth process.

28 The RTWCG rates in A4:Pd solutions we found to be highly  
29 preferential for silicon wafers with various crystallographic  
30 orientation. For example, the growth rate is up to 15 fold  
31 higher for (111) Si compared to (100) Si, and up to 4 fold for  
32 (110) Si compared to (100) Si. The chemical composition of the  
33 above oxides is Si-rich SiOX, as revealed by XPS data. In Table  
34 1 are shown some quantitative XPS data, including the position,  
35 normalized areas and the atomic concentration of the main

components of the oxide, recorded after sputtering about 30 nm from the surface of the 89 nm thick oxide.

Table 1. Quantification Table for Experiment A4: Pd-12. Sputtered 30 nm.

Peak	Center (eV)	SF	Norm. Area	[AT]%
F 1s	686.5	1.00	4.67676	0.401
O 1s	532.0	0.66	507.31055	43.463
Pd 3d	342.5	4.60	0.61422	0.053
C 1s	283.5	0.25	67.43414	5.777
Si 2p	99.5	0.27	587.19482	50.307

The oxidation rate in the A4: Pd solution of (111) a n-Si substrate, under the dark is much smaller compared to that of p-Si. Under about 100 mW/cm<sup>2</sup> visible light, the "growth" rate on n-Si was about the same, compared to the p-Si substrate. For both conductivity type (111) Si substrates, the thickness of the underlying Si substrate removed, is up to 25% of the oxide thickness, which suggests that a chemical oxidation reduction process is responsible for the formation of the chemical oxide. The A4: Pd solution was also tried for growing SiO<sub>x</sub> layers on (100) and (110) Si substrates. As mentioned above, the growth rates in these cases were much lower than that on (111) Si substrates. Because of this, on (100) Si substrates, the oxide grows preferentially at the defect areas, which reveal the (111) planes. This art-effect can be used for a non-destructive and very precise way to reveal the surface defects type and density on (100) Si surfaces.

Higher RTWCG rates of SiO<sub>x</sub> dielectric layers are recorded in mild BS based solutions, when pH is kept between 4 and 9. In this case, the difference between the growth rates on various crystallographic orientation, doping type and majority carrier concentration of Si surfaces are relatively small. For similar crystallographic orientations at similar carrier concentrations, in the dark, the growth rate is from 5% to 8% larger for p-type B-doped substrates compared to n-type P-doped substrates. For

similar doping type and doping concentrations there exist slight differences in the growth rates on Si substrates of different crystallographic orientations. The growth rate on (111) p-type B-doped Si with  $(N_A - N_D)$  of about  $2 \times 10^{19} \text{ cm}^{-3}$ , was found to be from 5 to 7% higher as compared to the growth rate on (100) p-Si of essentially similar carrier concentration.

Fig. 2 is a XPS surface survey of an RTWCG SiO oxide (112 nm thick), grown on p-type Si in BS-B15 solution. The growth solution was made by mixing 2 volume parts of 34% HSiF<sub>3</sub>, 2 volume parts of 5% n-BPCl aqueous solution, 1 volume part 0.5 M KOH aqueous solution, and with 0.3 g M KFeCN/100 ml solution. The growth time was 4 minutes, and the growth rate of 38 nm/min. For an oxide thickness of 235 nm, the growth rate was of about 35 nm/min. Table 2 gives some XPS data recorded at the surface of the oxide in Fig. 2.

Table 2. Quantification Table for Experiment BS-B15. Sputtered 30 nm.

Peak	Center (eV)	SF	Norm. Area	[AT]%
Fe 2p3	707.5	10.54	2.74384	0.063
F 1s	688.5	4.26	8.30465	0.189
O 1s	532.5	2.85	1947.9851	44.43
N 1s	399.0	1.77	13.91553	0.317
K 2s	373.5	1.95	0	0
C 1s	284.5	1.00	126.72832	2.89
Si 2p	102.5	0.87	2284.70996	52.11

The oxide above can be ascribed as Si-rich SiOX with C, Fe, N and F contaminants. No K has been detected at the surface. After sputtering 30 nm from the surface of the sample, Fe, C and Si concentrations decreased to 0.038%, 1.93%, and 50.26%, respectively, while the F, N, and O concentrations increased to 0.34%, 0.65%, and 46.78%, respectively.

Quantitative XPS analysis of oxides grown on p-Si using basic BS solutions indicates that the carbon contained at the surface of the oxide layer is a factor of 1.5 to 2 times greater, while the Fe and F contaminants decrease by a factor of 5 to 10

1 when  $\text{NH}_4\text{F}$  solutions is added to the KOH solutions. However, the  
2 growth rate of  $\text{NH}_4\text{F}$  based solutions, decreases quite  
3 significantly compared to the KOH based solutions. Adding NaF  
4 solutions further decreases the deposition rate, without  
5 increasing F contamination. Fig. 3 is a XPS surface survey of an  
6 RTWCG SiOX oxide (about 12 nm thick), grown on p-type Si in  
7 BS-B19 solution. The BS-B19 growth solution was made by mixing  
8 5 volume parts of 34%  $\text{HSiF}$ , 3 volume parts of 5% n-BPCl aqueous  
9 solution, 3 volume parts of 0.5 M KOH, 1 volume part each of 0.1  
10 M  $\text{NH}_4\text{F}$  and 0.1 M NaF aqueous solutions, and with 0.5 g M  
11  $\text{KFeCN}/100$  ml solution. The growth time was 6 minutes, and the  
12 growth rate was only about 2 nm/min. Fig. 4 shows the depth  
13 profile of this oxide. At the surface of the SiO-rich oxide, C  
14 replaces Si. The C concentration decreases from about 8.3% at the  
15 surface to near zero at the oxide/Si interface. The N  
16 concentration increases from 0.27% at the surface of the oxide  
17 to about 1.5% at the oxide/Si interface. The large surface C  
18 concentration and relatively large N interface concentration  
19 might explain the excellent chemical, UV and thermal stability,  
20 and, respectively, the excellent surface passivation capability  
21 of this oxide as shown in Example 5.

22 Our experimental data show that thin film RTWCG SiOX based  
23 oxides can be grown on porous silicon (PS) and the use of these  
24 coatings increase the stability of PS material against aging.  
25 RTWCG thin film SiOX layers are relatively easy grown on PS in  
26 both mild acidic and mild basic BS solutions. In a preferred  
27 embodiment of the invention, the growth solution BS-PS6 was made  
28 by mixing 5 volume parts of 34%  $\text{HSiF}$  with 3 volume parts of 5%  
29 n-BPCl aqueous solution, 3 volume parts of 0.5 M KOH, 1 volume  
30 part 0.1 M NaF aqueous solutions. Then 0.2 g  $\text{KFeCN}/100$  ml  
31 solution is added. The solution is agitated until complete  
32 dissolution of the  $\text{KFeCN}$  crystals. Fig. 5 is a surface survey of  
33 a SiOX coated PS. The PS was formed chemically on a (100) p-Si  
34 substrate, by the known process of stain etching using a solution  
35 based on HF and  $\text{HNO}_3$ . Then, a RTWCG SiOX thin film was grown on

1 the PS surface using the above, BS-PS6 solution. Table 3 gives  
2 XPS data recorded at the surface of the oxide in Fig. 5.

3 Due to the topography of the PS surface, the growth rate has  
4 only been estimated from the color code to be from 40 nm/minute  
5 to 50 nm/minute. The growth rate on planar p-Si substrates, using  
6 the BS-PS6 solution was at least 3 times smaller compared to the  
7 estimated growth rate on PS. Furthermore, differences exist in  
8 the chemical composition of the two oxides, grown on planar and  
9 PS using similar p-Si substrates. For instance, the C surface  
10 concentration of a 52 nm thick oxide grown on planar Si was 9.6%,  
11 compared to 36.5% at the surface of the oxide grown on PS. Also,  
12 the F concentration at the surface is about twice on PS compared  
13 to the planar surface. Although not very accurate, due to its  
14 surface topography, after 180 seconds sputtering, which  
15 corresponds to the removal of about 30 nm, the Si, C, and O  
16 concentrations became 39.283%, 18.895%, and 37.803% respectively.  
17 At the same depth the Fe, and F concentrations decreased to 0.11%  
18 and 0.646% respectively, while the N concentration became 0.443%.  
19 The origin of the Cu 2p3 line is unknown. Since it does not  
20 appear in the oxide grown on the planar Si, Cu could have been  
21 introduced into the PS during the stain etching step. This seems  
22 to be the case since the Cu concentration after the 180 sec.  
23 sputtering has increased to 2.821%. The role of Cu, if any, in  
24 the above differences observed in the composition of the oxides  
25 grown on PS and planar Si, deserve further investigation.

26 High RTWCG rates of SiO<sub>x</sub> dielectric layers of up to 64  
27 nm/minute according to this invention are possible using mild  
28 basic BS based solutions, when pH is kept between 7 and 9. One  
29 way to increase the growth rate is to use H<sub>2</sub>TiF<sub>6</sub> or TiCl<sub>4</sub> or  
30 (NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> into the growth solution. For example the BS:Ti  
31 solutions, using H<sub>2</sub>TiF<sub>6</sub> to enhance the grow rates of RTWCG SiO<sub>x</sub>  
32 oxides on Si are made of 3 to 5 volume parts of 34% HSiF mixed  
33 with 0 to 4 volume parts of 5% n-BPCl aqueous solution, 1 to 3  
34 volume parts of 0.1 M NH<sub>4</sub>F, 0 to 2 volume parts of 0.1 M NaF  
35 aqueous solutions and 0.5 to 2 volume parts of 60% H<sub>2</sub>TiF<sub>6</sub>. Then

0.1 to 1 g KFeCN/100 ml solution is added. The solution is agitated until complete dissolution of the KFeCN crystals.

Table 3. Quantification Table for Experiment BS-PS6. Surface.

Peak	Center (eV)	Norm. Area	[AT]%
Cu 2p <sub>3</sub>	934.5	11.049	0.495
Fe 2p <sub>3</sub>	710.0	4.6986	0.21
F 1s	688.5	35.543	1.592
O 1s	532.5	702.095	31.439
N 1s	399.0	0	0
K 2s	373.5	0	0
C 1s	284.5	815.133	36.501
Si 2p	102.5	664.650	29.763

Fig. 6 is a XPS surface survey of an RTWCG SiO oxide (about 70 nm thick), grown on p-type Si in BS-Ti34 solution. This growth solution was made by mixing 5 volume parts of 34% HSiF with 2 volume parts of 5% n-BPCl aqueous solution, 1 volume part each of 0.1 M NH<sub>4</sub>F and 0.1 M NaF aqueous solutions, 2 volume parts of 60% H<sub>2</sub>TiF<sub>6</sub>, and 1 g/KFeCN/100 ml solution. The larger than needed H<sub>2</sub>TiF<sub>6</sub> and KFeCN amounts in this example were chosen to study the oxidation stage of Ti and Fe included into the grown oxide. The growth time was 75 seconds, and the thickness of the oxide was 70.4 nm, and therefore the growth rate was of 56.3 nm/min. An oxide, grown simultaneously in the same solution, but extracted after 5 minutes had a thickness of 285 nm, that is a growth rate of 57 nm/minute. Table 4 gives XPS data recorded after sputtering 13 nm from the surface of the oxide in Fig. 6.

Table 4. Quantification Table for Experiment BS-Ti34. Sputtered 13 nm.

Peak	Center (eV)	Norm. Peak Area	[AT]%
Fe 2p <sub>3</sub>	706.81	86.426	10.516
F 1s	688.5	28.363	3.451
O 1s	532.5	296.168	36.035
Ti 2p	397.4	31.531	3.836
N 1s	284.5	28.220	3.434
C 1s	284.5	89.368	10.874
Si 2p	102.5	261.813	31.855



1 A depth profile of the above oxide components was acquired.  
2 At the surface the Fe, C and N concentration were about 11.5%,  
3 38%, and 27%, respectively. Within the top 26 nm, their  
4 concentration steadily decreased to below 2% each, and their  
5 concentrations continued decreasing to zero toward the oxide/Si  
6 interface, except for the N, which still had a concentration of  
7 0.58% near the interface. The Ti and F concentrations had a  
8 minimum at the surface of the oxide, e.g. 2.6% (Ti) and 0.15%  
9 (F), then their concentrations steadily increased to 40 nm, where  
10 they had a maximum of 4.8% (Ti) and 4.4% (F), and their  
11 concentration decreased steadily toward the interface, F with a  
12 larger rate. The large Ti and Fe concentrations should not  
13 recommend this oxide for most device applications, except if the  
14 Ti and Fe exist as oxides. A closed examination of Fe 2p<sub>3</sub>, and  
15 Ti 2p peaks (Fig. 7a, and Fig. 7b), suggest that toward the  
16 surface of the oxide Ti and Fe are a mixture of metallic and  
17 oxide components. However, toward the oxide/Si interface both  
18 Ti and Fe appear to be completely in an oxide form.

19 The foregoing and other objects, features and advantages of  
20 the invention will be apparent from the following more particular  
21 examples of preferred embodiments of the invention.

22 EXAMPLE 1. Low dielectric constant SiO<sub>x</sub> thin films for  
23 intermetallic dielectric (IMD) and interlevel dielectric (ILD)  
24 for ultra large scale integrated (ULSI) silicon based  
25 microelectronics.

26 Integrated circuit miniaturization continues to well below  
27 the half-micron level in the quest for higher speed and greater  
28 efficiency. At such reduced dimensions, the relatively high  
29 dielectric constant and resulting capacitance of conventional  
30 interlayer dielectric materials work to limit signal speed,  
31 create cross-talk and consume excessive power.

32 In the last two decades or so, there has been a continuous  
33 search for an alternate gate dielectric to SiO<sub>2</sub> grown by thermal  
34 oxidation, needed for a series of applications such as the high

1 speed, high performance large scale integrated (LSI), very large  
2 SI (VLSI) and ultra large SI (ULSI) circuit processes. The search  
3 continues for alternate to  $\text{SiO}_2$  layers and process technologies  
4 for 0.25  $\mu\text{m}$  and beyond microelectronics. The high-density plasma  
5 CVD (HDP-CVD) deposited SiOF has already been used to fill 0.35  
6  $\mu\text{m}$  gaps, and is also a contender for the 0.25  $\mu\text{m}$  and even for the  
7 0.18  $\mu\text{m}$  gaps, although it has proven very difficult to implement  
8 even for the 0.25  $\mu\text{m}$  gaps due to problems associated with the  
9 chemical-mechanical planarization (CMP) process. Hence, a  
10 selective growth of SiO-based films for fully planarized  
11 multilevel interconnections so as to eliminate the CMP process  
12 is very attractive for VLSI and ULSI device applications.

13 For 0.25  $\mu\text{m}$ , 0.18  $\mu\text{m}$ , 0.13  $\mu\text{m}$ , 0.10  $\mu\text{m}$  and beyond, work is  
14 under development on a variety of materials that can provide  
15 dielectric constants between 2 and 3 (e.g. fluorinated polyimides;  
16 non-polyimide C-H polymers; fluoro-polymers; siloxane polymers and  
17 parylenes, to name a few). All of these materials are just now  
18 beginning to be fully characterized, and, so far, the biggest  
19 common concern is their relatively poor thermal stability.  
20 The main disadvantages of conventional insulating films for VLSI  
21 (ULSI) applications include:

22 poor compatibility with multilevel interconnection,  
23 postdeposition planarization introduces stress, as well as  
24 chemical and particle contamination  
25 relatively poor thermal, UV, and plasma stability.  
26 high temperature; low growth (deposition) rate  
27 relatively poor step coverage,  
28 high investment cost

29 Using the RTWCG process and mild basic (pH from 8 to 9) BS  
30 solutions we were able to grow SiOX insulator layers on 2 to 4  
31 inch (100) and (111) p-Si and n-Si substrates. These insulator  
32 layers have:

33 a thickness from about 0.01 to 0.90  $\mu\text{m}$  (as determined from  
34 ellipsometry)  
35 a growth rate of up to 64 nm/min.

1 measured static dielectric constant between 2.95 and 4.8  
2 very good uniformity  
3 good chemical and thermal stability

4 In Fig. 8 are given plots of ellipsometric data of selected  
5 five SiOX chemical oxides. For comparison, also are given plots  
6 for a thermally oxidized SiO<sub>2</sub> and resistive evaporated SiO,  
7 respectively grown/deposited on similar p-Si substrates.

8 In developing the WCG processes for room temperature growth  
9 of SiOX based insulators, the chemical composition and the  
10 chemical structural features of the liquid molecules must ensure  
11 the proper length, reactivity, permanent dipole momentum and  
12 surface tension so allow uniform growth of stable oxide layers  
13 of controllable composition and thickness. For example because  
14 the insulator film is grown in liquid state, if the liquid  
15 precursors of the growth solution are properly selected, the  
16 surface tension forces inside spaces with critical features of  
17 0.25  $\mu$ m and beyond and high aspect ratio will pull the film flat  
18 - a selfplanarization effect. This is extremely important for  
19 developing self-planarizing growth processes of intermetallic  
20 dielectric films, interlevel dielectrics, and shallow trench  
21 isolation of ULSI Si-based micro- and nano-electronics.

22 The above requirements necessitate complex interdisciplinary  
23 theoretical and experimental studies of fluid dynamics,  
24 electrochemistry, physics of the interfaces, etc. For instance,  
25 the flow and range of interaction forces between complex liquids  
26 and the nanostructure surfaces cannot be solved by the known  
27 dynamic and kinetic-molecular theories of liquids. Moreover, the  
28 Laplace type forces, determined by the internal fluid pressure,  
29 are drastically modified by the physical-chemical interactions  
30 of complex liquid molecules with the surfaces of the  
31 nanostructures with various geometries.

32 We have been able to prove that the RTWCG SiOX oxide layers  
33 can be made compatible with metallization schemes, including Cu  
34 and Ag, and photoresists. Due to its excellent gap filling

capability, this room temperature process could become the process of choice for fully planarized multilevel interconnections for ULSI microelectronics with high aspect ratio and features size of 100 nm and beyond, for which none of the presently known techniques seem to work.

For measuring the static dielectric constant, we fabricated MOS capacitors using RTWCG SiOX oxides. For the fabrication of Al/as-grown RTWCG oxide/p-type Si/Au:Ti MOS capacitors (with gate areas from  $2 \times 10^{-4} \text{ cm}^2$  to  $2 \times 10^{-3} \text{ cm}^2$ ), the SiOX oxides were grown after the ohmic back contacts were made, and no further annealing steps were used in the fabrication of MOS capacitors. We also fabricated MOS capacitors using thermal SiO<sub>2</sub> so as to check the validity of our measured values. The thickness of the SiOX and SiO<sub>2</sub> layers was measured using a Dektak profiler.

Table 5 gives the solution growth, the oxide thickness for the reference thermal SiO<sub>2</sub> and selected RTWCG SiOX oxides, the average refractive index (400 to 800 nm wavelength range) as determined from ellipsometry, and the static dielectric constant, measured at 1 MHz.

Table 5. Static dielectric constant vs. average refractive index in the visible spectra (1 = 400 to 800 nm) for RTWCG SiOX oxides grown on (100)p-Si. Growth time: 4 to 25 minutes.

Solution	Oxide Thickness (nm)	Av. Refractive Index	Dielectric Constant
Thermal SiO	108	1.492	3.95
BS:B15	208	1.365	3.08
BS:PS6	107	1.353	2.95
A4:Pd	135	1.492	4.33
BS-Ti34	801	1.542	~ 4.80

EXAMPLE 2. RTWCG of SiOX thin films for gate dielectric for ULSI silicon based microelectronics.

In the last two decades or so, there has been a continuous search for an alternate gate dielectric to SiO<sub>2</sub> grown by thermal oxidation, needed for a series of applications such as the high

1 performance ULSI. The  $\text{SiO}_2$  has already been replaced by slightly  
2 modified  $\text{SiO}_2$ , i.e. oxynitrides.

3 For the development of electronic devices with critical  
4 features below 100 nm, the thickness of the insulator layers has  
5 to be scaled down accordingly, but retain its passivating and  
6 dielectric properties. As an example, for use as a gate  
7 dielectric of modern MOS transistors the oxide thickness will be  
8 in the range of 6-10 nm for 0.35  $\mu\text{m}$  generation technologies and  
9 will scale to less than 4 nm for 100 nm and beyond technologies.  
10 To our knowledge none of the already developed or recently  
11 proposed insulator layers would satisfy the technological  
12 requirements of high-speed, low-power nanoelectronics with  
13 critical features of below 100 nm.

14 Based on our preliminary investigation the RTWCG SiOCN oxide  
15 grown in solution BS-B19 (see Fig. 3 and Fig. 4), could be a good  
16 candidate for use as a gate insulator for low-power, high-speed  
17 integrated nanoelectronics. The growth rate of this oxide on  
18 (100) p-Si substrates is only about 2 nm/minute, which should  
19 allow a good thickness control of the growth of 4 to 6 nm thick  
20 oxides. The large surface C concentration and relatively large  
21 N interface concentration might explain the excellent chemical,  
22 UV and thermal stability, and, respectively, the excellent  
23 surface passivation capability of this oxide. Although we have  
24 not yet measured it, based on its chemical composition and  
25 ellipsometric data, we estimate ultra thin film SiOCN oxides  
26 would have a dielectric constant lower than 3.

27 EXAMPLE 3. SiO-based insulator for surface passivation for  
28 photonic (optoelectronic) device applications.

29 If the insulating layer is deposited directly on the Si  
30 surface, it is imperative that it provides good passivation of  
31 the surface. This is an important aspect, very often overlooked  
32 in developing insulator layers. This is difficult to achieve for  
33 future IC electronic and optoelectronic structures with shrinking  
34 feature size using traditional dielectric growth/deposition  
35 techniques. Based on our preliminary data, if well controlled,

1 the SiOX oxides grown by the new RTWCG technique will have better  
2 passivating properties of Si surfaces compared for example to  
3 inorganic and organic spin-on glasses because the chemical growth  
4 should result in uniform and well-defined noncrystalline layers  
5 with short range order.

6 As mentioned in Example 2, the RTWCG SiOCN oxide grown in  
7 solution BS-B19 has excellent chemical, UV and thermal stability,  
8 and, respectively, excellent surface passivation capability. Its  
9 passivating qualities we tested on some n+p Si solar cells. Using  
10 solution growth BS-B19 and a growth time of 4 minutes, we grew  
11 a 72 nm thick SiOCN oxide on two 4cm<sup>2</sup> Si solar cells. On one of  
12 these cells we recorded a gain of 63.2% in short circuit current  
13 density ( $J_{sc}$ ), e.g. from 23.69 mA/cm<sup>2</sup> (bare surface) to 38.66  
14 mA/cm<sup>2</sup>. This gain was much larger than that expected from the  
15 decrease in the reflectivity. For another cell, in similar  
16 conditions, we recorded a gain in  $J_{sc}$  of 62.8% (oxidized  
17 simultaneously with the cell above). After removing the oxide  
18 from the surface of the first cell, the  $J_{sc}$  became 32.1 mA/cm<sup>2</sup>,  
19 compared with the initial value of 23.69 mA/cm<sup>2</sup>. This relative  
20 increase of about 36.5% we attribute to surface passivation of  
21 this bare Si cell, which means that the increase due to the  
22 difference in reflection is only about 27%. This is comparable  
23 or better with reported increases in  $J_{sc}$  using a single layer AR  
24 coating.

25 EXAMPLE 4. SiO-based insulator for use as a single layer  
26 antireflection coating for Si-based planar solar cells.

27 The anti-reflective (AR) coating is one of the most  
28 important parts of a solar cell design, as it allows a  
29 substantial reduction in the amount of reflected light. For Si,  
30 the loss of incident light amounts to 34% at long wavelength (1.1  
31  $\mu$ m) and rises to 54% at short wavelength (0.4  $\mu$ m). A proper  
32 single layer AR coating can reduce the reflection to about 10%,  
33 averaged over this wavelength range, and a double layer AR  
34 coating can reduce it to around 3% on the average.

1       It is a common practice to use physical vapor deposition  
2 techniques to deposit the AR coating. For simple cell structures,  
3 the layers of AR coating are deposited directly onto the emitter  
4 surface by resistive or e-beam evaporation, sputtering and  
5 chemical vapor deposition. The most common single layer AR  
6 coatings are  $\text{MgF}_2$ ,  $\text{SiO}_2$ ,  $\text{SiO}$ ,  $\text{TiO}_2$  and  $\text{Ta}_2\text{O}_5$ . For high efficiency  
7 space solar cells, the most commonly used double layer AR coating  
8 is  $\text{ZnS/MgF}_2$ . All of the above deposition methods are known to  
9 destroy the stoichiometry at the cell's front surface, which, by  
10 increasing the scattering at the grain boundaries, decreases the  
11 AR coating/semiconductor interface transparency and introduces  
12 additional defects at the emitter/AR coating interface. For this  
13 reason, high efficiency III-V based space solar cells use a  
14 window layer grown on the surface of the emitter prior to  
15 depositing the layers of the AR coating. This window layer  
16 partially reduces the degradation effects mentioned above.  
17 Lattice-matched window layers are grown by epitaxy; this  
18 increases the cost and reduces the yield of finished cells.  
19 Radiation induced defects at the window/emitter layer interface  
20 is an additional concern for the design engineers of space solar  
21 cells.

22       We started a preliminary investigation to test the overall  
23 quality of large growth rate RTWCG SiOX oxides using BS solutions  
24 such as BS:B15, BS:B19, and BS-Ti34 by using them as  
25 passivation/first layer AR coating for planar Si cells.

26       For our preliminary study we used several dozens readily  
27 available planar  $2 \times 2 \text{ cm}_2$  n/p Si solar cells with AMO,  $25^\circ\text{C}$   
28 efficiency of about 7% (bare cells). Before the measurements,  
29 the front surfaces of the bare cells were cleaned with organics,  
30 followed by a short dip into a 2% HF solution. RTWCG SiO-based  
31 coatings were then grown in the BS-Ti34 chemical system.

32       The variation in external quantum efficiency of one such  
33 bare cell before (a) and after the RTWCG SiOX oxide grown in the  
34 BS-Ti34 chemical system (b) is shown in Fig. 9.

The performance parameters, a selection of which are given in Table 6, were measured at NASA LeRC prior to and after the coatings, under AMO, 25°C conditions.

Table 6. AMO, 25°C performance parameters of selected 2x2 cm<sup>2</sup> n/p Si cells prior to (bare) and after RTWCG of SiO-based coatings in the BS-Ti34 chemical system. Growth time: 3 to 5 minutes; thickness: 95 to 120 nm; No annealing.

Cell	Bare Cell				Coat. Cell				$(\eta_{ox} - \eta_{bare}) / \eta_{bare} (\%)$
	$I_{sc}$ (mA)	$V_{oc}$ (mV)	FF (%)	$\eta$ (%)	$I_{sc}$ (mA)	$V_{oc}$ (mV)	FF (%)	$\eta$ (%)	
Cox 12	89.2	583.9	75.2	7.16	118.0	579.5	75.0	9.45	32.0
Cox 27	88.0	573.1	70.4	6.49	117.2	572.7	71.8	8.81	35.7
Cox 23	88.3	570.9	68.7	6.33	119.9	571.0	69.5	8.69	37.3

After the SiO-based coatings, the only treatment the cells received prior to the AMO measurements was rinsing them into DI water and drying them in N<sub>2</sub>. The large increase in the efficiency of these cells, after the RTWCG SiO-based coatings, are due to a very good optical quality of coatings grown in the BS-Ti34 chemical system. However, although the passivating property of this coating is better than that of some commercial AR coatings, it is not yet as good as that of coatings grown in the BS:B15 and BS:B19 chemical systems. The reason for this is the relatively large amounts of metallic components (Ti in this example), which still exist in the high refractive index interfacial M-O rich Si-O-X layer, as revealed by the XPS spectra, such as the one shown in Fig. 7a. The SiOX oxide used for cell "12" in Table 6 was grown in identical conditions as the one in Fig. 6. The coating used for cell "23" had a lower concentration of metallic Ti, compared to cell "12" as revealed by the better defined TiO<sub>x</sub> peaks, with a smaller shoulder toward the metallic Ti.



1           As seen in Table 5, by varying the chemistry of the solution  
2 growth it is possible to deposit SiOX AR coatings with tailorable  
3 index of refraction by including various amounts of Ti-O and N-O  
4 groups into the SiOX layer. RTWCG of SiOX coatings is possible  
5 on surfaces with existing metallization such as with grid fingers  
6 on solar cell or thermophotovoltaic (TPV) cell surfaces.  
7 Therefore, once metallization has been done on the cell, and  
8 after chemical removal of nonstoichiometric front surface layers,  
9 insulating WCG SiOC coatings can be used for the dual purpose of  
10 surface passivation and as AR coating.

11           Note that  $I_{sc}$  values for the cells in Table 6, increase  
12 significantly after RTWCG of SiO-based coating, while the  $V_{oc}$   
13 values remain practically unchanged. The explanation might have  
14 to do with the fact that the surfaces of the 10-15 years old  
15 planar cells could not be properly cleaned, prior to growing the  
16 SiO-based coating, without removing some or all front grid  
17 fingers. For these cells, using mild acidic solutions of the  
18 BS:B15 type chemical system, it should be possible in one step to  
19 remove the nonstoichiometric (dead) front surface layer,  
20 passivate the surface, and grow a good quality AR coating.

21           EXAMPLE 5. RTWCG SiOX based insulators for use as a  
22 passivating/single layer antireflection coating for Si-based  
23 concentrator vertical multijunction (VMJ) silicon solar cells.

24           Light-induced effects in the Si/insulator interface are  
25 known to adversely affect the solar cell performances. Although  
26 these light-induced effects affect especially surface sensitive  
27 devices such as the silicon inversion layer solar cells, these  
28 effects have also been reported for high efficiency silicon  
29 point-contact solar cells after extended exposure to concentrated  
30 sunlight. The light-induced degradation is due to the generation  
31 of fast surface states at the silicon/insulator interface. For  
32 terrestrial solar cell applications this effect can be minimized,  
33 since cover glass and suitable encapsulants act as a filter  
34 cutting off the energetic wavelengths ( $\lambda < 335$  nm) which are  
35 mainly responsible for light induced degradation of solar cell.

1 performances. For concentrator solar cells in general and  
2 point-contact and VMJ Si solar cells in particular, however,  
3 these effects cannot be neglected.

4 Vertical MultiJunction (VMJ) Si solar cells, (US patent #  
5 4,332,973; 4,409,422, and 4,516,314) show a good promise for use  
6 as concentrator solar cells. One of the biggest challenge in  
7 fabricating high efficiency, stable VMJ cells is the difficulty,  
8 using traditional techniques, to passivate the two back and front  
9 surfaces, and the two non-metallized edge surfaces.

10 For this preliminary experiment some early Vertical  
11 MultiJunction (VMJ) Si solar cells were provided to us by the VMJ  
12 Si solar cell developer, PhotoVOLT, Inc. The biggest contributor  
13 to efficiency loss in the Si VMJ cell structure is the fact that  
14 its illuminated and back surfaces, and the two edge surfaces  
15 uncovered by metallization, are high recombination surfaces with  
16 exposed junctions that are difficult to passivate. Also,  
17 traditional AR coatings are difficult to form on these cells  
18 because of temperature constraints and because of their  
19 configuration with the four exposed surfaces. The RTWCG process  
20 grows SiO<sub>2</sub>-based oxides simultaneously on the four exposed  
21 surfaces. These coatings, grown at room temperature, are easy  
22 to apply, are stable, passivate well the VMJ Si cell surfaces,  
23 and act as an effective AR coating. Some results are given in  
24 Table 7.

25 Table 7.  $I_{sc}$  and  $V_{oc}$  of two VMJ Si cells after chemical  
26 passivation (by PhotoVOLT) of bare cells, and after RTWCG of SiO<sub>2</sub>  
27 coatings. Growth time: 4 minutes; Oxide thickness: about 120  
28 nm. No annealing.

Cell	Bare Cell		Coat. Cell		( $I_{sc,ox} - I_{sc,bare}$ ) / $I_{sc,bare}$ (%)	( $V_{oc,ox} - V_{oc,bare}$ ) / $V_{oc,bare}$ (%)
	$I_{sc}$ (mA)	$V_{oc}$ (V)	$I_{sc}$ (mA)	$V_{oc}$ (V)		
PV 414	0.398	12.57	0.52	14.22	30.7	13.1
PV 412 (Side 1)	0.385	13.31	0.56	14.55	45.6	9.3
PV 412 (Side 2)	0.425	13.17	0.57	13.95	34.1	5.9

Notes: VMJ Si solar cells with their multiple (16 to 40) exposed junctions are probable the most surface sensitive solar cells. The biggest contributor to efficiency loss in the Si VMJ cell structure is the fact that its illuminated and back surfaces are high recombination surfaces with exposed junctions (up to 40) which are difficult to passivate. After the SiOX coatings, the only treatment the cells received prior to the AMO measurements was rinsing them into DI water and drying them in  $N_2$ . The RTWCG SiOX coated VMJ cells surpassed the performances and UV stability of cells with resistively evaporated  $Si_3N_4$ , SiO and  $Ta_2O_5$  AR coatings. We attribute this to the intrinsic good passivating and optical quality of the RTWCG Si-O-C-N oxide.

On some Si VMJ cells with  $Ta_2O_5$  as an AR coating, after 1 hour exposure to high intensity (about 50 mW/cm<sup>2</sup>) near UV light, the drop in the performance parameters was as high as 20%. After the exposure, the cell performance parameters completely recovered after only about 30 minutes, which suggests that fast surface states at the  $Ta_2O_5$ /Si interface were responsible for the performance parameters drop. After removing the  $Ta_2O_5$  layer, passivating the surfaces using a RTWCG SiOCN oxide (solution BS-B19), the cell performance parameters increased by as much as 50%. Additionally, no UV degradation was observed even after

1 exposure to the aforementioned halogen light for as long as 5  
2 hours. In fact, for some cells, with similar surface treatments,  
3 measurements performed in the PV branch at NASA LeRC under AM0,  
4 25°C conditions, showed even a small increase in performance  
5 parameters after prolonged light exposure.

6 For solar cell and especially surface sensitive solar cell  
7 applications, such as vertical multijunction (VMJ) solar cells,  
8 the surface recombination velocity has to be made as small as  
9 possible. This means that metallic and carbon impurities, have  
10 to be kept a low concentration at the oxide/semiconductor  
11 interface. This means the amount of Fe or Ti present in some of  
12 our SiOX oxides should be kept at a very low level. In order to  
13 preserve a low SRV, our experimental results show that high  
14 growth rate solutions such as BS-Ti34 can be used, however the  
15 UV stability of VMJ cells coated with SiOX using this solution  
16 is not as good as when BS:PS6 or BS:B15 or BS:B19 solutions were  
17 used.

18 EXAMPLE 6. SiO-based insulator for use as passivating films  
19 for porous silicon coated photonic (optoelectronic) devices.

20 Chemical stabilization of the PS material and conservation  
21 (or enhancement) of the luminescence efficiency are two current  
22 challenges confronting the development of porous-silicon-based  
23 photonic (optoelectronic) device applications.

24 As is known, good chemical stability is obtained upon  
25 oxidizing the PS surface, either thermally or by anodic  
26 oxidation. But this does not appear as a promising route for  
27 device application, because this impedes electrical carrier  
28 injection. On a single-crystal planar silicon surface, the  
29 hydride passivated surface is known to exhibit a fair stability  
30 against oxidation and contamination, at least on a time scale of  
31 a few hours. In contrast, the PS surface is much more prone to  
32 oxidation and contamination, and, especially for high porosity  
33 samples, the infrared spectra exhibit traces of contaminated  
34 native oxide formation, after a few tens of minutes in air. On  
35 the other hand, on flat silicon crystals, methoxylation of the

1 surface has been reported as a key factor in order to account for  
2 the long-term stability and the low interfacial recombination  
3 characteristics in methanol-based photoelectrochemical cells.  
4 Similar modifications of the porous silicon surface then appears  
5 highly attractive since it might provide a much more stable  
6 surface which could be used as a processing step for device  
7 applications. In a recent study after formation of PS in  
8 concentrated HF electrolyte, methoxy groups were formed through  
9 partial anodic dissolution of the hydrogenated PS surface in  
10 anhydrous methanol. The methoxylated surface exhibited improved  
11 optical characteristics (increased photoluminescence efficiency  
12 and blue shift of the emission), similar to PS anodically  
13 oxidized in a nonfluoride aqueous electrolyte. Its stability  
14 against aging was also improved as compared to that of the  
15 hydrogenated surface, but without reaching the stability of  
16 anodically oxidized PS. The relative instability is ascribed to  
17 the amount of SiH species, which remain, on the methoxylated  
18 surface upon the modification process.

19 Basic properties of PS, such as photoluminescence (PL)  
20 origin, formation mechanism, and structure, have been extensively  
21 studied. Meanwhile, the fundamentals of PS devices are being  
22 developed. It is important to develop a corresponding device  
23 technology for PS that is compatible with the conventional  
24 integrated circuit technology. For example, a key step in the  
25 fabrication of PS devices and integrated optoelectronic circuits  
26 is the formation of light emitting patterns. This is a difficult  
27 process because any postprocessing will seriously affect the  
28 properties of PS due to its porous, fragile, and chemically  
29 reactive structure. A research team from the University of  
30 Rochester and the Rochester Institute of Technology, N.Y. have  
31 managed for the first time to integrate a PS light emitting diode  
32 (LED) into a conventional microelectronics device" (Semiconductor  
33 International, January 1997). The LED is said to be 10,000 times  
34 more efficient than the first PS Si LED, fabricated in 1990. The  
35 improvements they are envisioning will further boost the

1 efficiency 10-fold and increase its frequency 100-fold. To  
2 achieve this, as a first step, we feel they should consider  
3 replacing the Si-rich  $\text{SiO}_2$  layer they are presently using with a  
4 better passivating layer and with a lower dielectric constant.  
5 The use of Si-rich  $\text{SiO}_2$ , although compared to  $\text{SiO}_2$  offers the  
6 advantage of better withstanding some postprocessing steps such  
7 as etching, it is not a good choice for surface passivation, has  
8 lower resistivity and dielectric strength, higher dielectric  
9 constant, and should be less stable with respect to plasma  
10 processing, UV and ionizing radiation.

11 Recently we started a very preliminary study on the  
12 possibility of increasing the stability of PS material against  
13 aging using RTWCG grown SiOCN-rich thin film coatings for  
14 photonic (optoelectronic) device applications, and in particular  
15 for low reflection passivated front surface formation for Si  
16 solar cell applications. The PS was formed chemically on (111)  
17 and (100) Si substrates, using a solution based on HF and  $\text{HNO}_3$ .  
18 Then, a RTWCG of thin SiOX layers were grown at room temperature  
19 (see Fig. 5). In Fig. 10 are shown reflectivity plots of: (a) RCA  
20 cleaned (100) p-Si wafer, (b) PS coated, (c) RTWCG SiOX  
21 passivated PS using A4:Pd solution (see Fig. 1), and (d) RTWCG  
22 SiOX passivated PS using BS-PS6 solution (see Fig. 5). As seen,  
23 the reflection of SiOX coated PS in curve (c) in the portion of  
24 the spectra of interest for solar cells is about 10%, while from  
25 580 nm to 1040 nm the reflectivity of SiOX coated PS in curve (d)  
26 is below 4%, which is equal or lower than that of best double  
27 layer AR coatings.

28 The RTWCG process of SiOCN layers on the PS surface, a room  
29 temperature process, appears highly attractive for photonic  
30 (optoelectronic) device applications, since it will provide a  
31 much more stable surface in reducing and oxidizing agents and  
32 with respect to factors such as heat, humidity, prolonged  
33 exposure to UV light, atomic oxygen and ionizing radiation during  
34 postprocessing steps and as a result of exposing the fabricated  
35 devices to such environments. Based on our preliminary work, it

1 appears that compared to planar silicon surfaces, good quality  
2 WCG SiOCN coatings are much easier to grow on PS coated Si  
3 surfaces. The reason for this is not fully understood at the  
4 present time.

5 While the invention has been particularly shown and  
6 described with reference to preferred embodiments thereof, it  
7 will be understood by those skilled in the art that other changes  
8 in form and details may be made therein without departing from  
9 the spirit and scope of the invention. For instance Fe-EDTA used  
10 in combination with KFeCN increase noticeable the growth rate of  
11 SiOX oxides grown in BS-Ti34, but the Fe contamination is  
12 slightly larger. From among large number of possible electronic  
13 and photonic (optoelectronic) device applications we have only  
14 mentioned the six above examples. It will be understood by those  
15 skilled in the art that any that these RTWCG SiOX oxides can be  
16 grown on other than Si semiconductor substrates, including Ge,  
17 III-V and I-III-VI compound semiconductors, and used for a wide  
18 range of electronic and photonic (optoelectronic) device  
19 applications without departing from the spirit and scope of the  
20 invention. Other applications described herein, which make use  
21 of various description of these oxides are also covered by this  
22 invention. One such example is given below.

23 Example 7. Novel optical technique for Si surface defect  
24 revealing.

25 We have mentioned that using the A4:Pd solution, the growth  
26 rate of SiOX oxides on (100) Si is much lower than that on (111)  
27 Si substrates. Because of this, on (100) Si substrates, the oxide  
28 grows preferentially at the defect areas, which reveal the (111)  
29 planes. This art-effect can be used for a non-destructive and  
30 very precise way to reveal the surface defects type and density  
31 on (100) Si surfaces. In other words, on (100) Si surface the  
32 oxide spots which grow preferentially at the dislocation areas  
33 can be used as an essentially nondestructive and very accurate  
34 technique for revealing the type and density of surface defects  
35 (e.g. etch pits, dislocations, and scratches). Using this

1 approach, we consistently recorded from 5 to 10% more surface  
2 defects as when using conventional preferential etching  
3 techniques. We found that when using the preferential etching  
4 techniques the larger the defect density the larger the error in  
5 defect density. This is so, since the larger pits, overlap over  
6 the smaller ones, which makes it difficult to accurately count  
7 their density. Using the new higher resolution technique of  
8 preferential oxidation, the defect areas are much better  
9 delineated and are much easier to visualize using any high  
10 magnification optical or electronic microscope. Using this  
11 technique, rapid and accurate automatic surface defects mapping  
12 is possible using either reflectivity, room temperature  
13 photoluminescence intensity or index of refraction imaging  
14 techniques. Because using the solution A4:Pd, the thickness of  
15 the underlying (100) Si substrate removed during the RTWCG  
16 process is less than 25% of the oxide thickness, and since less  
17 than 40 nm thick oxide is needed to easy visualize the oxide  
18 spots by any of the above optical techniques, it means that the  
19 thickness of the removed material at the dislocation sites is  
20 less than 10 nm. This makes this novel technique essentially  
21 nondestructive, which should recommend it for large volume  
22 process control in Si wafer and device industries.



What is claimed:

1           1. A method for forming a silicon oxide-based layer on a  
2 semiconductor substrate, said method comprising:  
3           providing a reaction mixture including  $\text{H}_2\text{SiF}_6$ ,  
4           n-n-butylpyridinium chloride, and a  $\text{Fe}^{2+}/\text{Fe}^{3+}$  aqueous  
5           reduction-oxidation solution; and  
6           reacting said mixture with said semiconductor substrate to  
7           form said silicon oxide-based layer.

1           2. A method according to claim 1, wherein said mixture is  
2 saturated with a substance including  $\text{SiO}_2$ .

1           3. A method according to claim 1, wherein said  $\text{Fe}^{2+}/\text{Fe}^{3+}$   
2 aqueous reduction-oxidation solution includes an aqueous solution  
3 of  $\text{K}_3\text{Fe}(\text{CN})_6$  or iron ethylenediaminetetraacetic acid.

1           4. A method according to claim 1, wherein said mixture  
2 further includes a catalyst selected at least partially upon the  
3 pH of the mixture.

1           5. A method according to claim 4, wherein palladium II  
2 trifluoroacetate is used as a catalyst when said mixture has a  
3 pH in the range of from about 4 to about 6.

1           6. A method according to claim 4, wherein at least one of  
2 dihydrogen hexafluorotitanate, titanium chloride  $\text{TiCl}_4$  and  
3  $(\text{NH}_4)_2\text{TiF}_6$  is used as a catalyst when said mixture has a pH in the  
4 range of from about 3 to about 9.

1           7. A method according to claim 1, wherein the pH of the  
2 mixture is adjusted with at least one of  $\text{NaOH}$ ,  $\text{NaF}$ ,  $\text{KOH}$ ,  $\text{NH}_4\text{F}$  and  
3  $\text{HF}$ .

1           8. A method for forming a silicon oxide-based layer on a  
2 silicon substrate, said method comprising:  
3           providing a reaction mixture including  $\text{H}_2\text{SiF}_6$ ,  
4           n-n-butylpyridinium chloride, and a  $\text{Fe}^{2+}/\text{Fe}^{3+}$  aqueous  
5           reduction-oxidation solution; and  
6           reacting said mixture with said silicon substrate to form  
7           said silicon oxide-based layer.

1           9. A method according to claim 8, wherein said mixture is  
2 saturated with a substance including  $\text{SiO}_2$ .

1           10. A method according to claim 8, wherein said  $\text{Fe}^{2+}/\text{Fe}^{3+}$   
2 aqueous reduction-oxidation includes an aqueous solution of  
3  $\text{K}_3\text{Fe}(\text{CN})_6$  or iron ethylenediaminetetraacetic acid.

1           11. A method according to claim 8, wherein said mixture  
2 further includes a catalyst selected at least partially upon the  
3 pH of the mixture.

1           12. A method according to claim 11, wherein palladium II  
2 trifluoroacetate is used as a catalyst when said mixture has a  
3 pH in the range of from about 4 to about 6.

1           13. A method according to claim 11, wherein at least one  
2 of dihydrogen hexafluorotitanate, titanium chloride  $\text{TiCl}_4$  and  
3  $(\text{NH}_4)_2\text{TiF}_6$  is used as a catalyst when said mixture has a pH in the  
4 range of from about 3 to about 9.

1           14. A method according to claim 8, wherein the pH of the  
2 mixture is adjusted with at least one of NaOH, NaF, KOH,  $\text{NH}_4\text{F}$  and  
3 HF.

1           15. A method for forming a silicon oxide-based layer on a  
2 silicon substrate, said method comprising:

3 providing a reaction mixture consisting essentially of  
4  $\text{H}_2\text{SiF}_6$ , n-n-butylpyridinium chloride, and a  $\text{Fe}^{2+}/\text{Fe}^{3+}$   
5 aqueous reduction-oxidation solution; and  
6 reacting said mixture with said silicon substrate to form  
7 said silicon oxide-based layer.

1 16. A method according to claim 15, wherein said mixture  
2 is saturated with a substance including  $\text{SiO}_2$ .

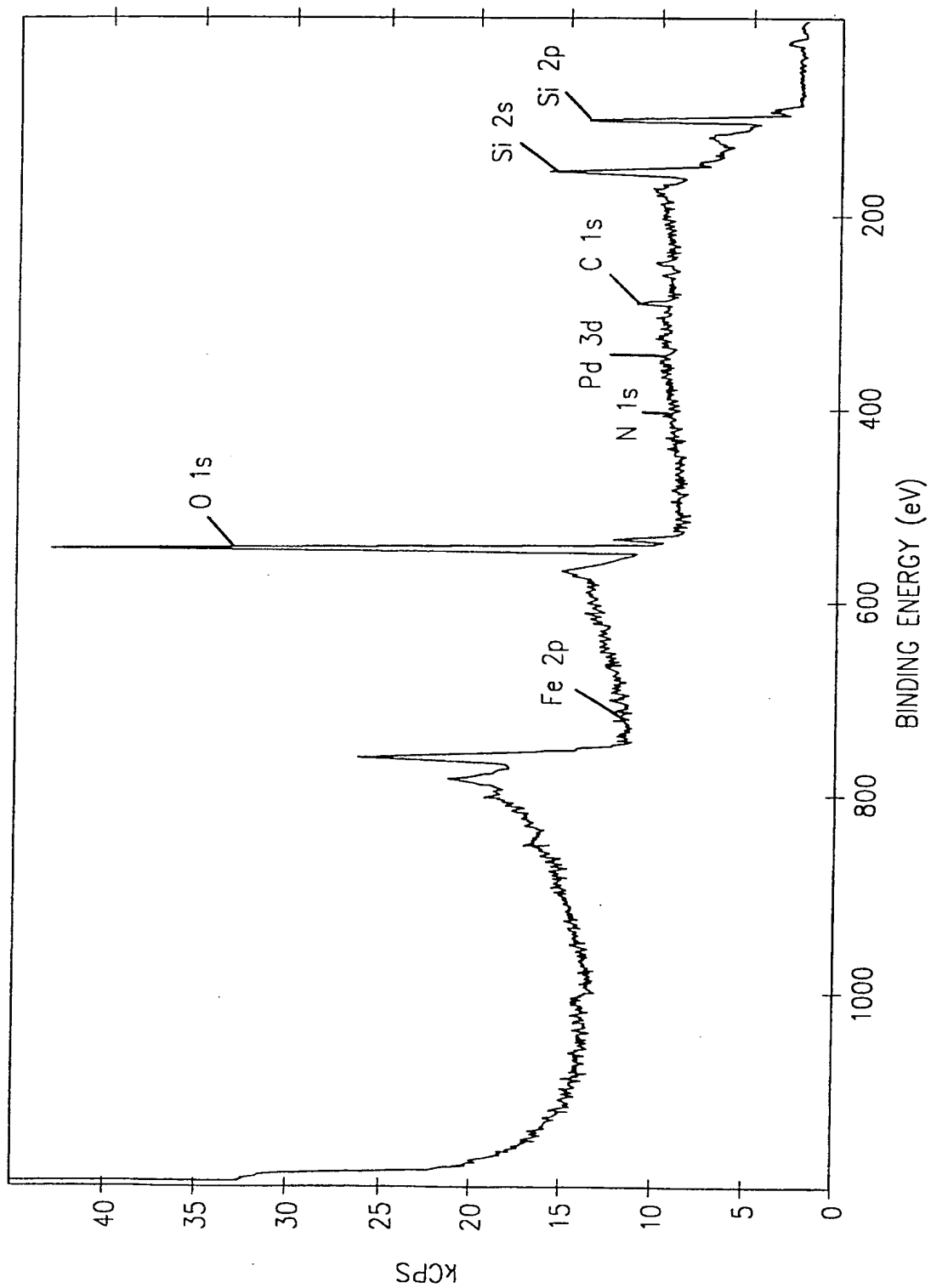
1 17. A method according to claim 15, wherein said  $\text{Fe}^{2+}/\text{Fe}^{3+}$   
2 aqueous reduction-oxidation solution includes an aqueous solution  
3 of  $\text{K}_3\text{Fe}(\text{CN})_6$  or iron ethylenediaminetetraacetic acid.

1 18. A method according to claim 15, wherein said mixture  
2 further includes a catalyst selected at least partially upon the  
3 pH of the mixture.

1 19. A method according to claim 18, wherein palladium II  
2 trifluoroacetate is used as a catalyst when said mixture has a  
3 pH in the range of from about 4 to about 6.

1 20. A method according to claim 18, wherein at least one  
2 of dihydrogen hexafluorotitanate, titanium chloride  $\text{TiCl}_4$  and  
3  $(\text{NH}_4)_2\text{TiF}_6$  is used as a catalyst when said mixture has a pH in the  
4 range of from about 3 to about 9.

1 21. A method according to claim 15, wherein the pH of the  
2 mixture is adjusted with at least one of NaOH, NaF, KOH,  $\text{NH}_4\text{F}$  and  
3 HF.

**FIG. 1**

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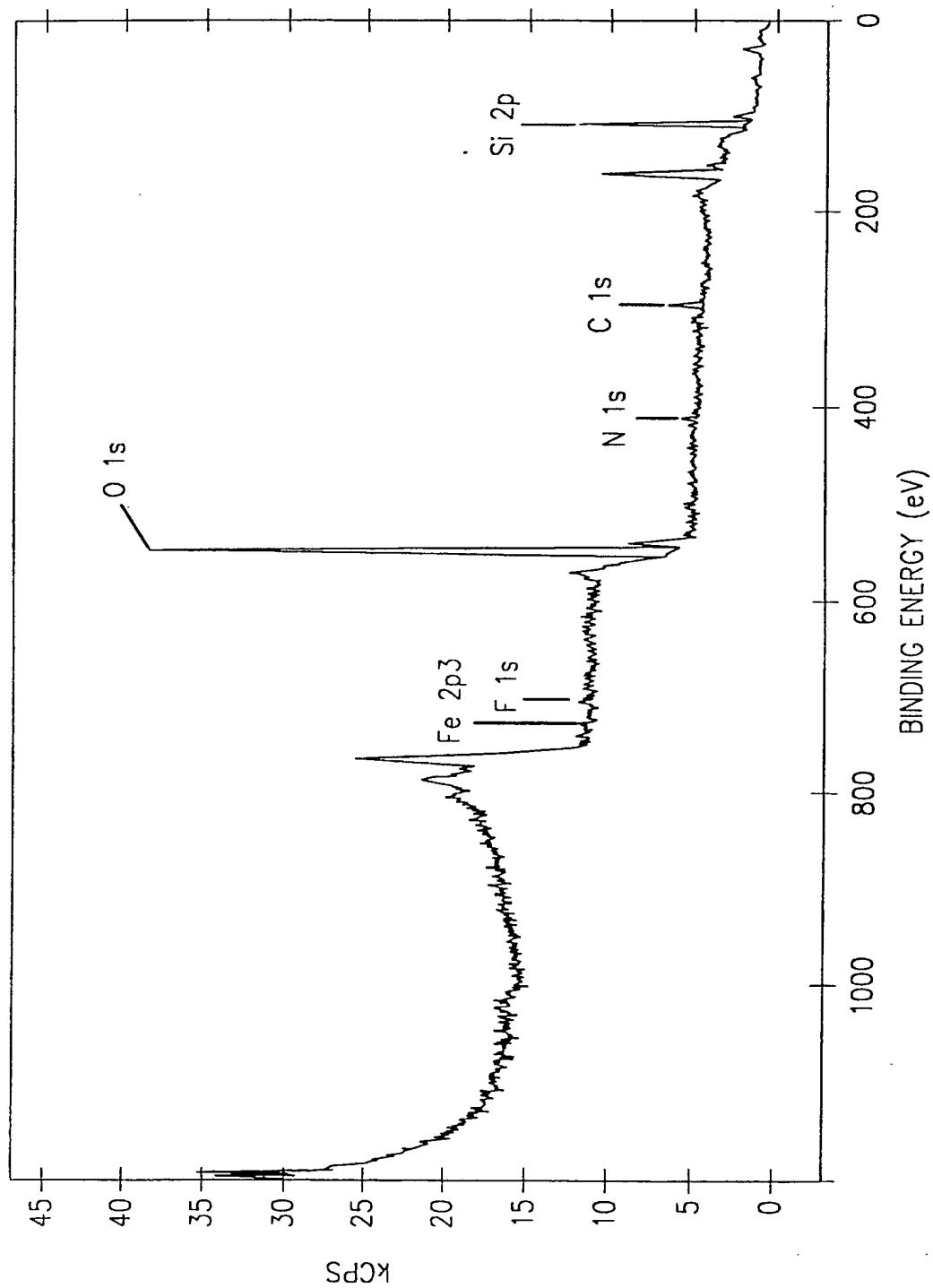
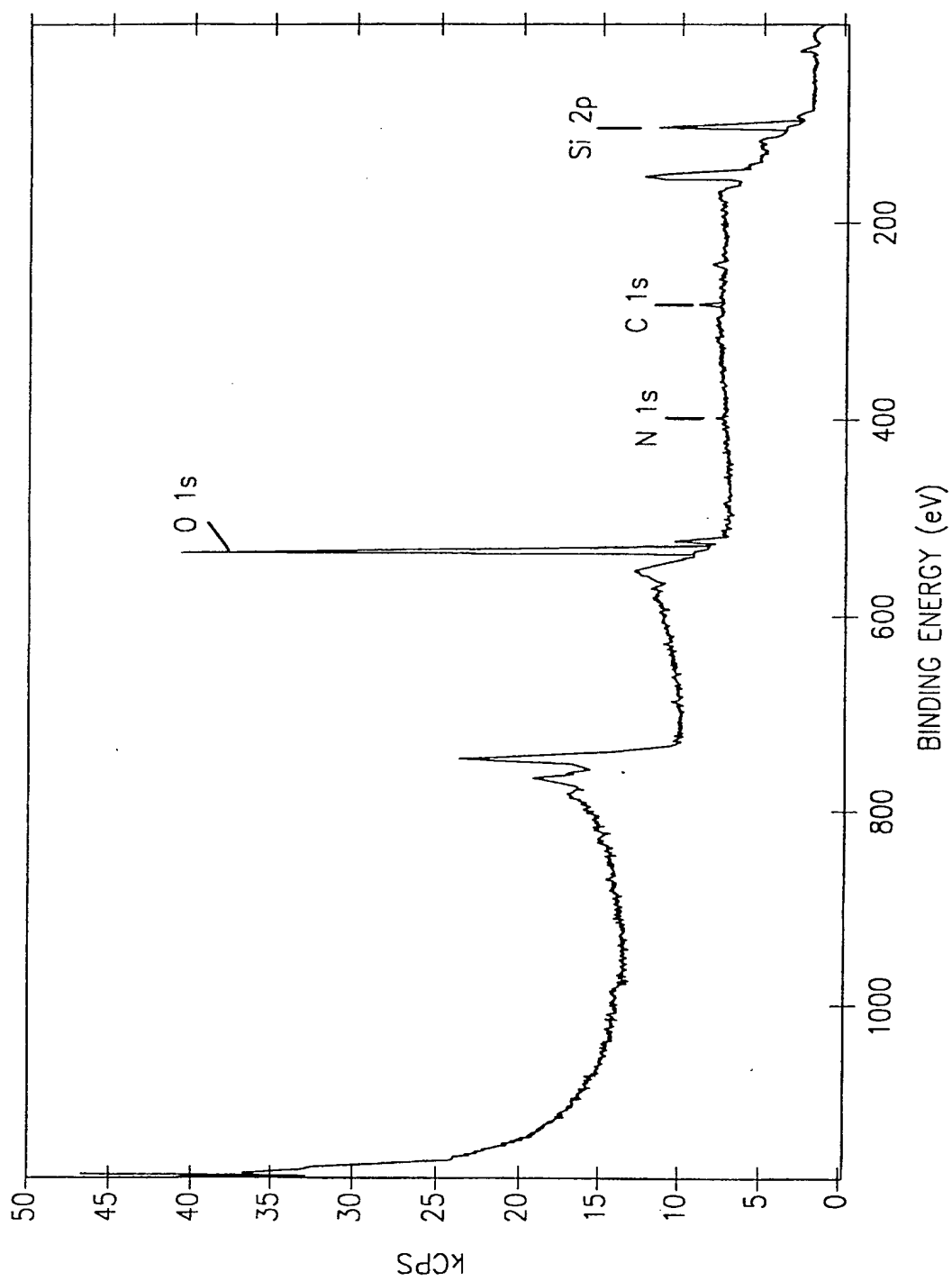


FIG. 2

**FIG. 3**

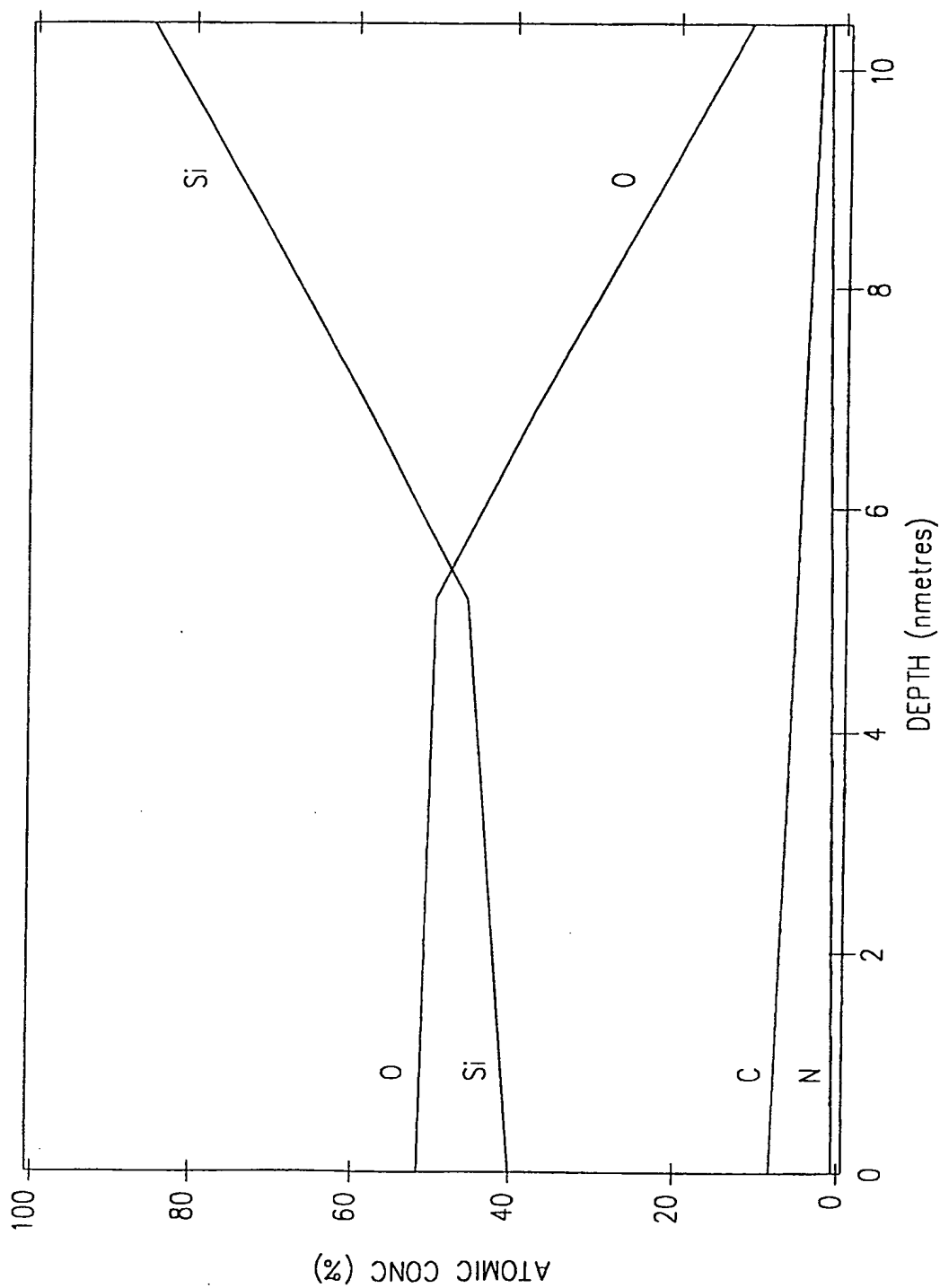


FIG. 4

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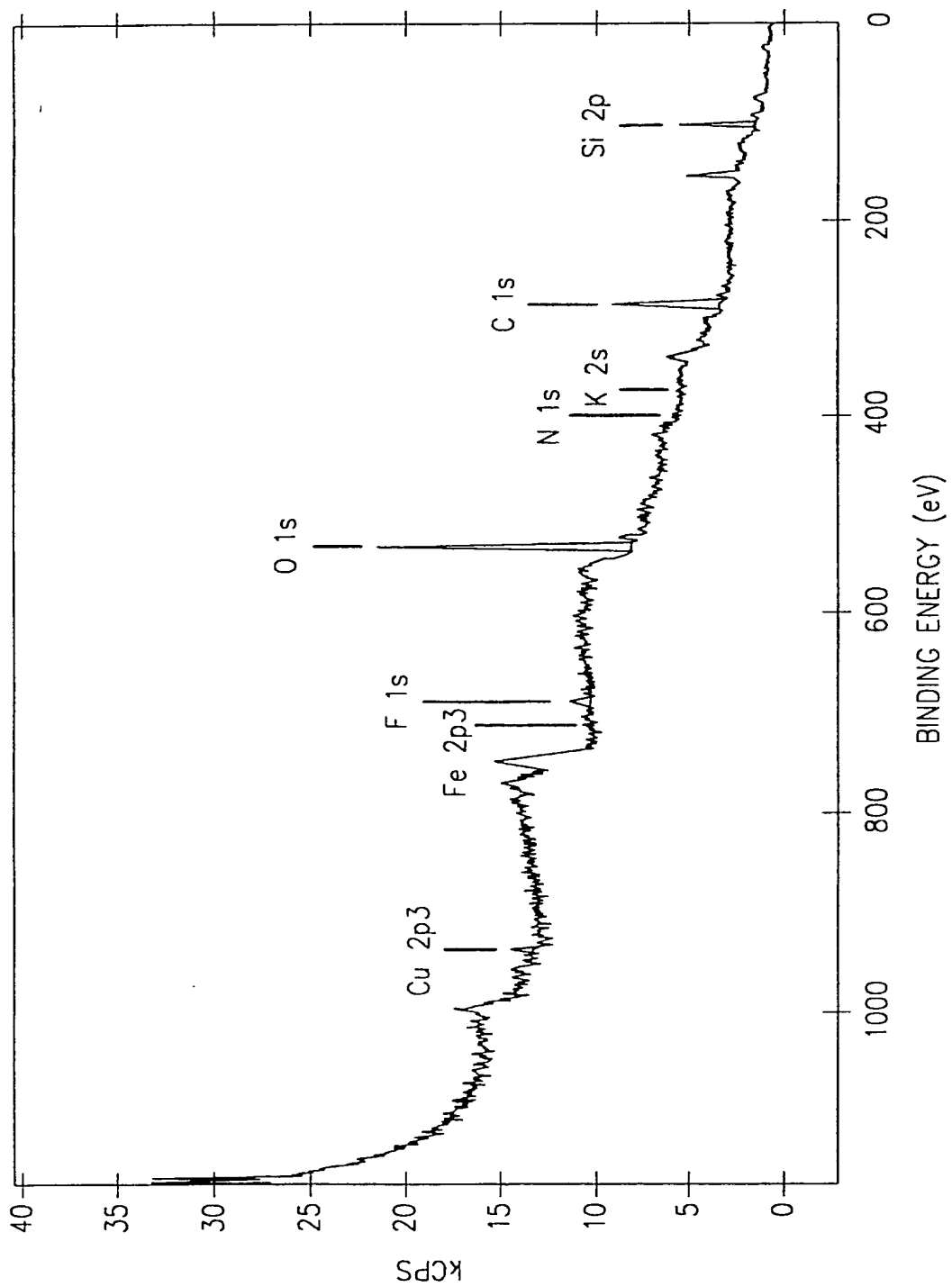
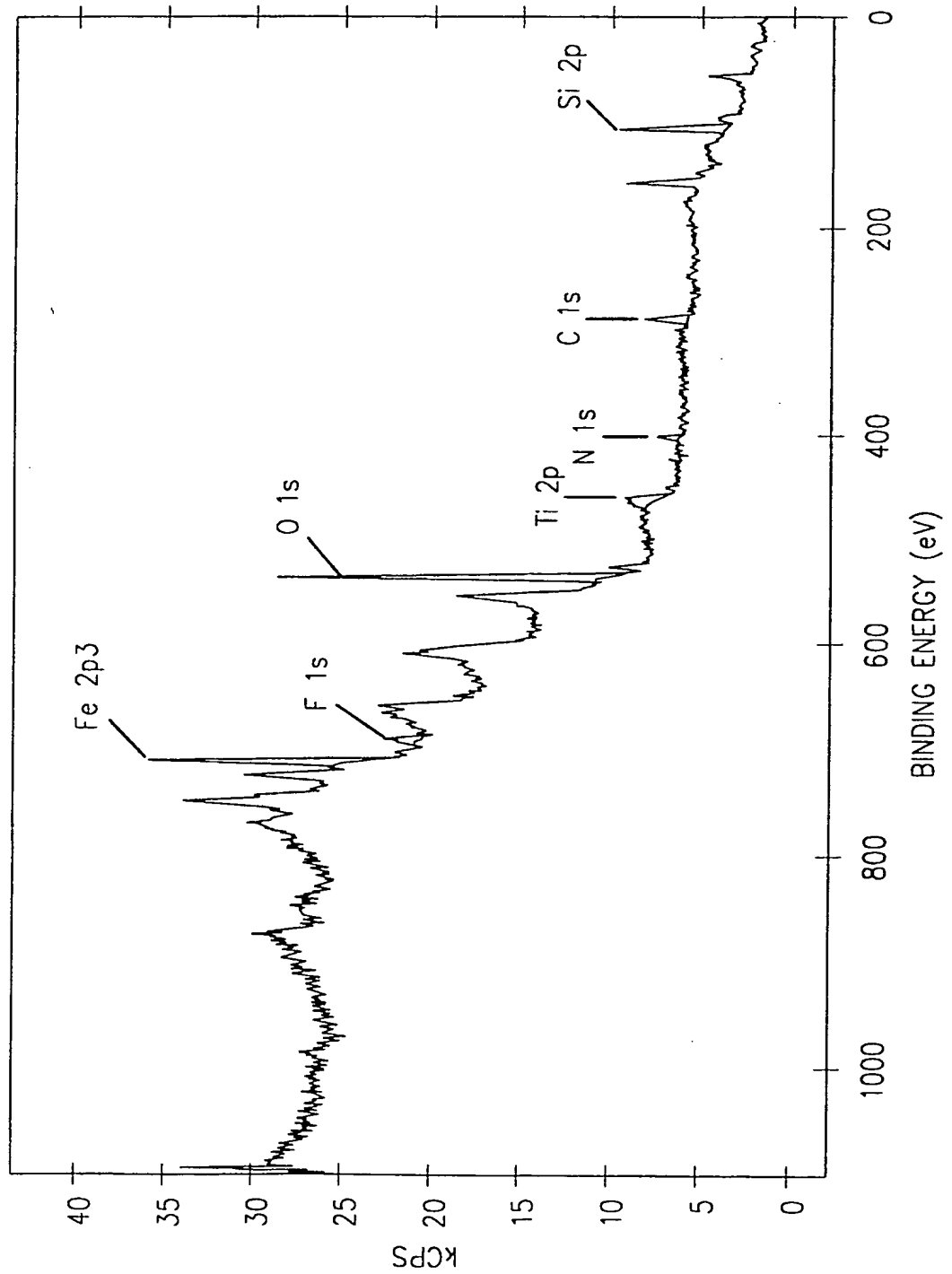


FIG. 5



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**FIG. 6**

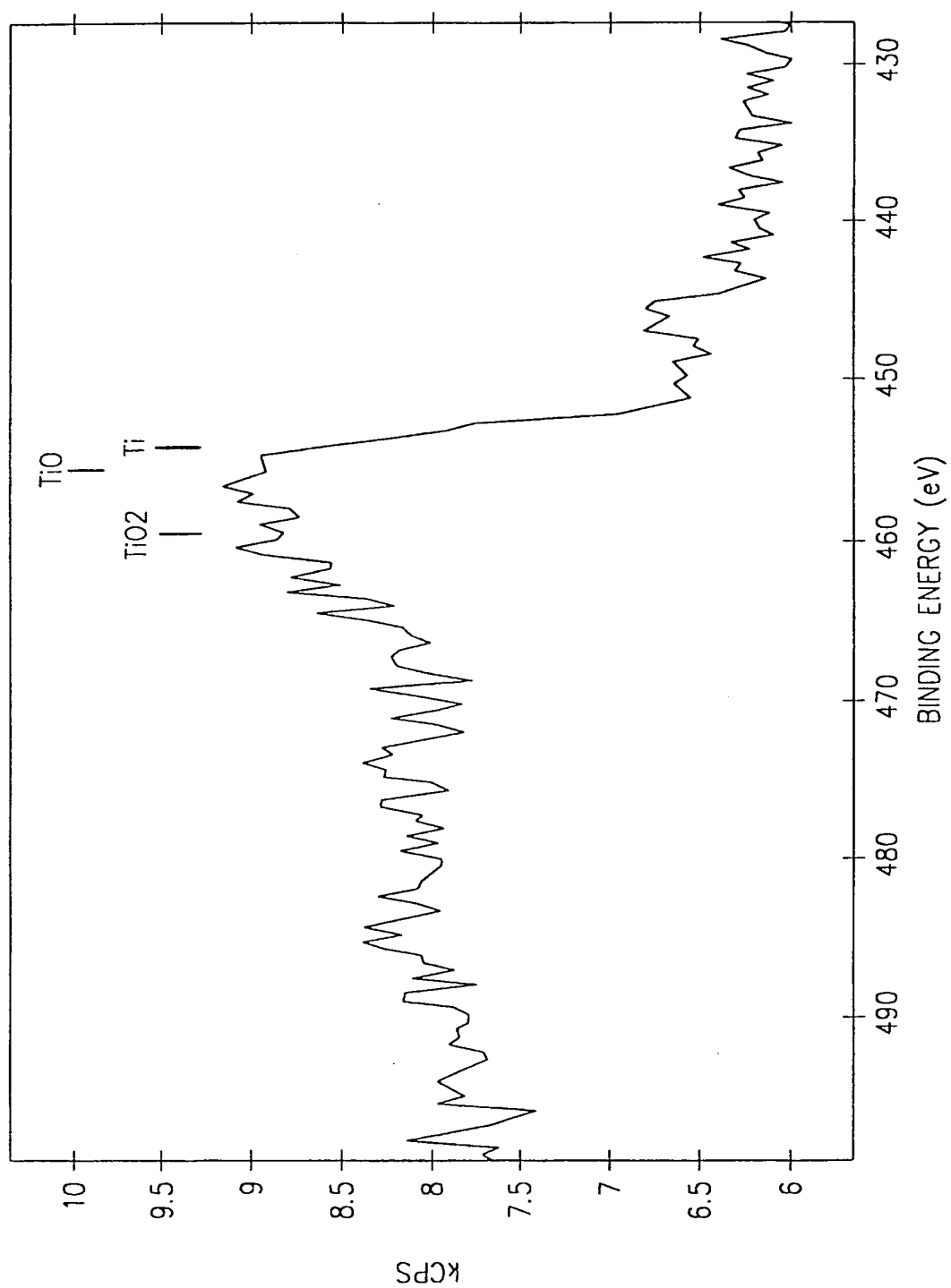
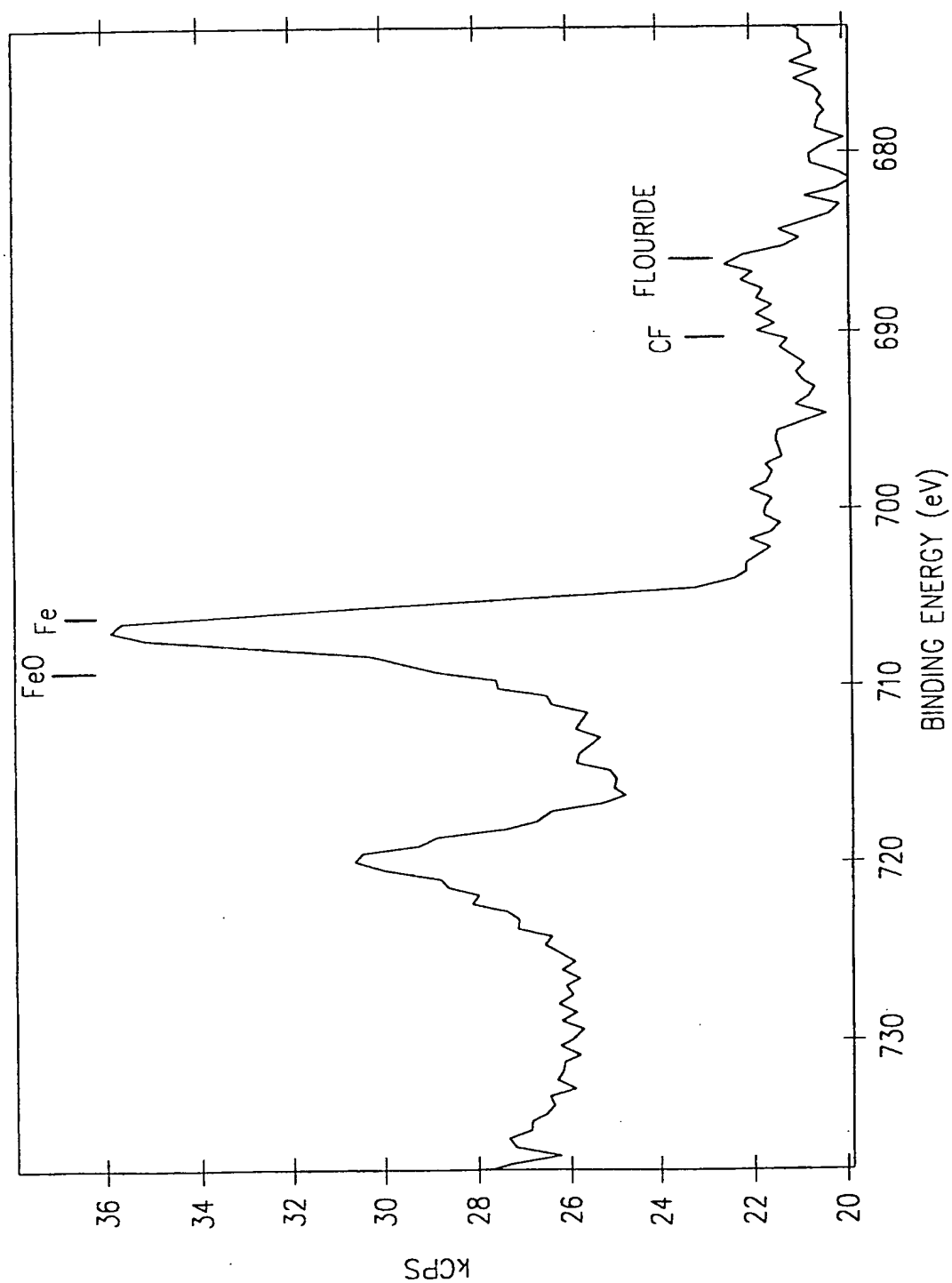


FIG. 7A

**FIG. 7B**

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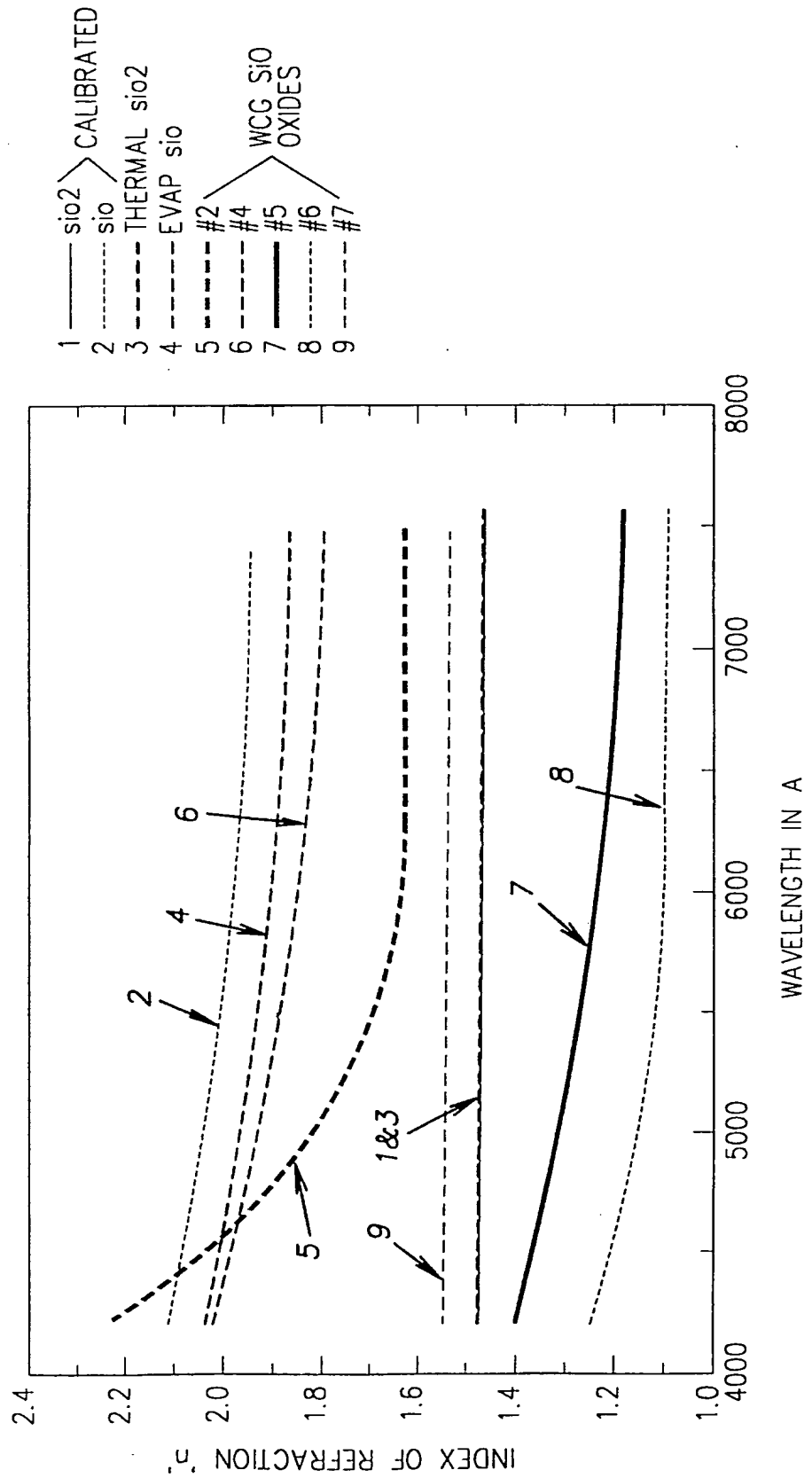


FIG. 8

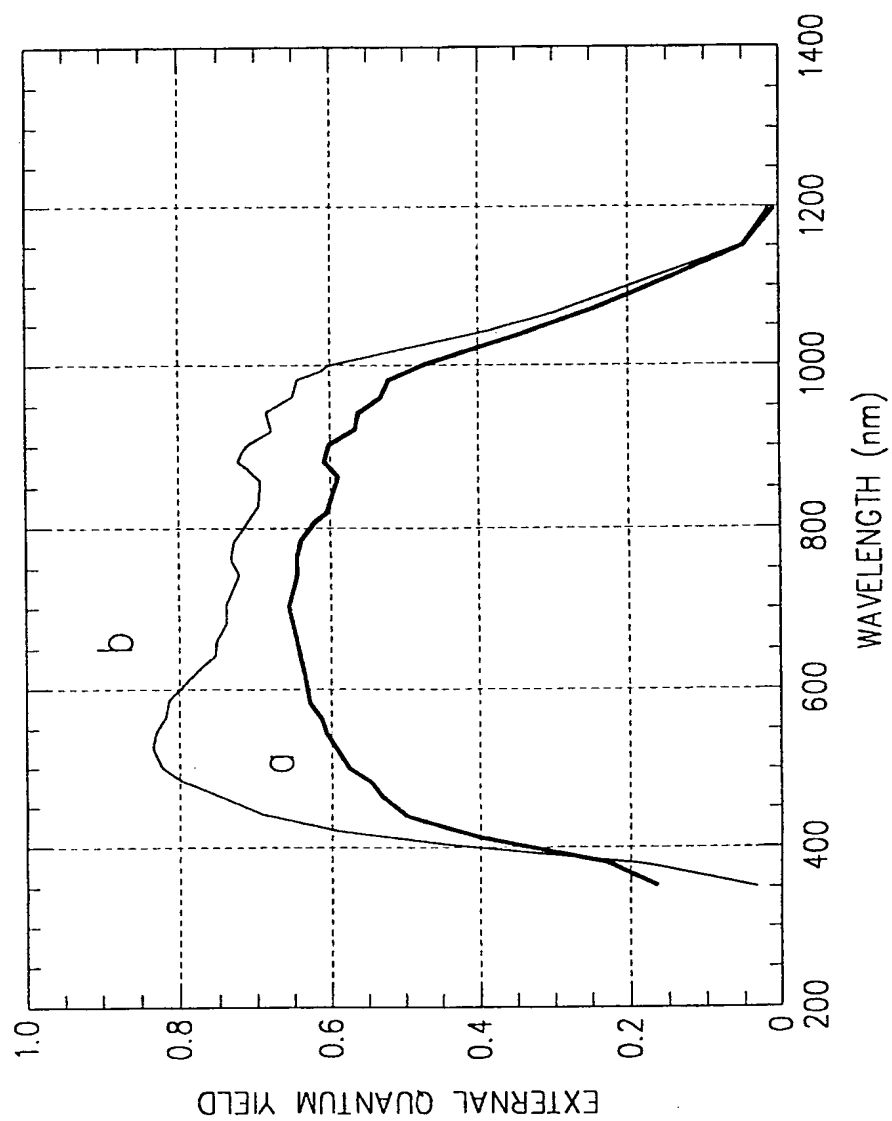


FIG. 9

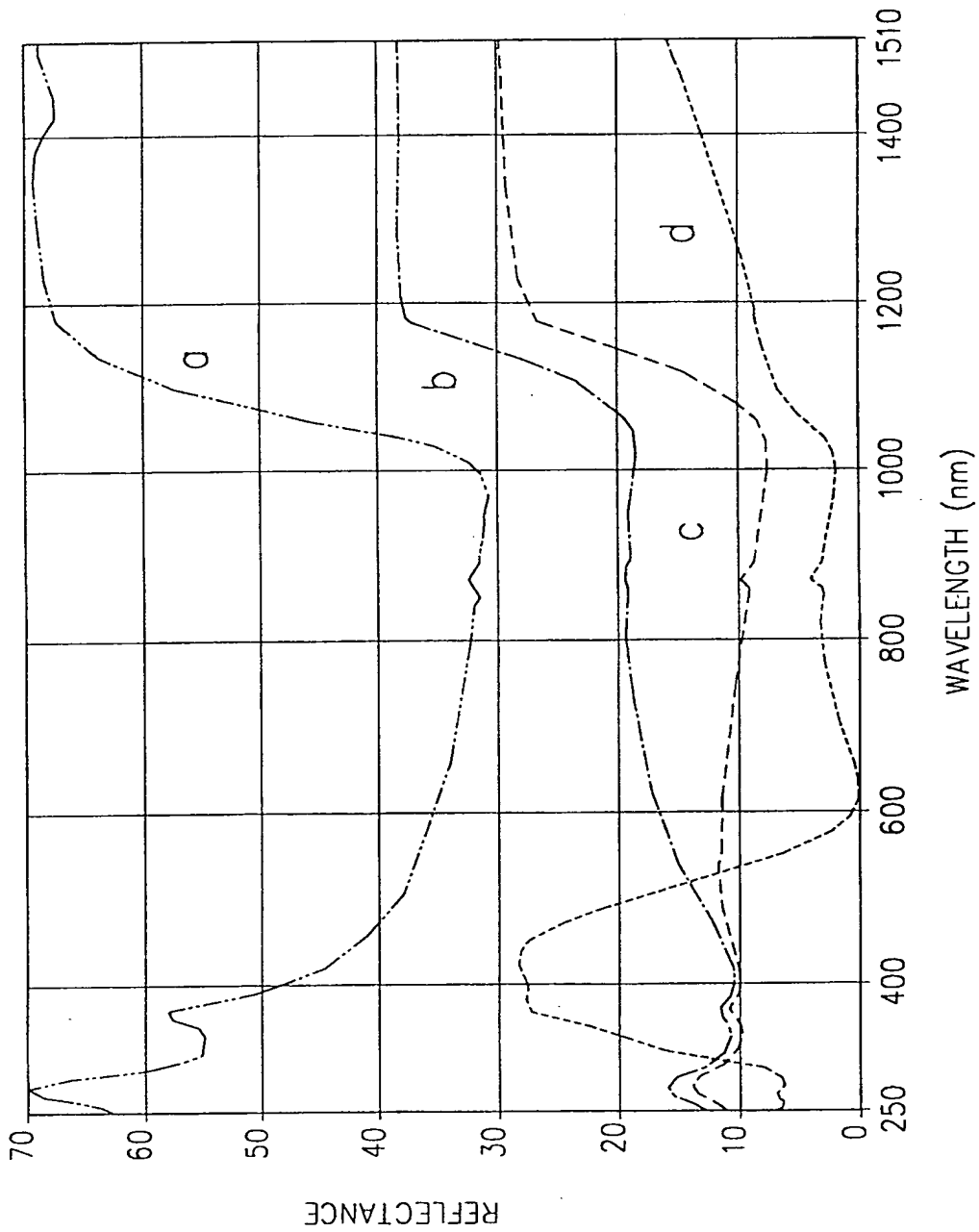


FIG. 10

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/07159

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H01L 21/31;

US CL :438/ 769, 770, 787, 789, 790;

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 438/ 769, 770, 787, 789, 790;

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
WEST, EAST

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,693,916A (NAGAYAMA et al) 15 September 1987 (15.09.87), col. 3, lines 1-25.	1-21

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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